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# A Volumetric Study of Aqueous Butanol Solutions

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A Volumetric Study of Aqueous Butanol Solutions


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## I.   Abstract

Alcohol molecules consist of two distinct regions: a polar, hydrophilic alcohol group, and an aliphatic hydrocarbon chain. These regions interact with solvent water molecules in different ways. While the alcohol group acts as a solvent structure breaker by hydrogen bonding with nearby water molecules, the hydrophobic carbon chain acts instead as a solvent structure maker and causes the surrounding water molecules to align themselves in a Clathrate structure. The presence of these two contrasting solute-solvent interactions affects the properties of the solution, among them the molar volume. The partial molar volume of the alcohol is analyzed with respect to three variables: the size and location of the hydrophilic moiety, the concentration of the alcohol-water solution, and the temperature at which the density measurement is made. We show that all three of these variables have a noticeable effect on the interactions between the solute and solvent molecules, and thus the volume of the solution.

## II.    Introduction

In recent years, this laboratory has engaged in a systematic study of solution structure using volumetric and refractometric measurements of solutions. For instance, Fucaloro et al. measured the densities and indexes of refraction for several aqueous monosaccharides and disaccharides at various temperatures to gain insight into the solvation region surrounding the solute. They determined that the water contained within the solvation sphere of the solute was denser than that of the bulk water. [1] Solutes that interact with water such that the solvated water is denser than bulk water are termed "solvent structure breakers," and those that cause the solvated water to be less dense than bulk water are "solvent structure makers." Benson et al. did a similar volumetric study of methanol, ethanol and 1-propanol, and found similar results. [2]

It is important to assess the solvation of hydrophobic and hydrophilic regions in organic molecules, particularly biomolecules. However, such a task can be difficult to accomplish when dealing with complex systems. To solve this problem, a simpler molecular system can be examined. These results can be applied to more complex systems, such as proteins or other large biomolecules. The vast majority of biomolecules contain both polar, hydrophilic portions and aliphatic, hydrophobic portions. An alcohol contains both while being a much simpler molecule to analyze, making it an excellent model.

Water molecules in an aqueous solution may develop one of two molecular solvent structures. The first is an "icelike" structure that forms due to a high degree of hydrogen bonding between water molecules. Pure water forms this solvent structure naturally. The second is a "collapsed" structure, where the extent of hydrogen bonding is less than the former. [3] Alcohols, which possess both hydrophilic and hydrophobic regions, are both solvent structure makers and breakers. The aliphatic portion is designated as the A region and the alcohol group the B region. Both the A region and the B region for each solute molecule have a certain number of water molecules surrounding them, signified as $q_A$ and $q_B$ respectively. As r increases, $q_A$ and $q_B$ both decrease, since the increased number of alcohol molecules results in a greater amount of overlap between

the regions of adjacent molecules, causing some water molecules to interact with multiple alcohols.

The molar volume of solvated water molecules around region A should be greater than that of pure water, since there would be a higher degree of hydrogen bonding. In contrast, the volume of solvated water molecules around region B should be less than that of pure water, because the increased amount of hydrogen bonding between water molecules and the hydroxyl group results in an increase in collapsed structure for the solvated water in this region.

### III.   Mathematical Treatment of Data

As the basis for our experimental data, the definition of some terms and calculations for data interpretation was required before any conclusions could be reached.

The equation used to find the molar volume V of a binary solution from its density $\rho$, as reported by Fucaloro et al., is:

$$V = \frac{n_1 M_1 + n_2 M_2}{\rho}$$

(1)

where $M_1$ and $M_2$ are the respective molar masses of solvent water and solute. [4]

The total volume of a solution is, as is the case for all total thermodynamic state functions, a homogeneous function of the amounts of the components. Following Euler, one may thus write

$$V_{tot} = n_1 V_1 + n_2 V_2$$

(2)

where $n_1$ is the number of moles of water and $n_2$ is that of alcohol, $V_1$ is the partial molar volume of water, namely $\left(\frac{\partial V_{tot}}{\partial n_1}\right)_{T,\ P,\ n_2}$ and $V_2$ is the partial molar volume of alcohol, $\left(\frac{\partial V_{tot}}{\partial n_2}\right)_{T,\ P,\ n_1}$

Dividing both sides of Equation 2 by $n_1$ gives the modified volume function V*, defined by Fucaloro et al. as

$$V^* = \frac{V_{tot}}{n_1} = \frac{V}{x_1} = \frac{M_1 + r M_2}{\rho} = V_1 + r V_2,$$

(3)

where r is the mole ratio of alcohol to water. [1]

For an ideal solution, $V_1$ and $V_2$ are constant with respect to concentration, and therefore with respect to the mole ratio of the solution. The ideal modified volume function may be written as

$$V^*_{ideal} = V_1^{\cdot} + rV_2^{\circ} \, ,$$

(4)

where $V_1^{\cdot}$ is the molar volume of pure water, and $V_2^{\circ}$ is the partial molar volume of the solute at infinite dilution.

$V_e^*$, the "excess" or non-ideal portion of $V^*$, can therefore be defined as

$$V_e^* = V^* - V^*_{ideal}$$

(5)

### IV.    Molecular Model for Solvation

To develop a molecular model for solvation, one can perform a stoichiometric analysis. For a binary system containing solvent water and a solute S, one solute molecule will interact with water to form $SW_q$, which represents the interaction of one solute molecule with a coordination number of water molecules $q$ around the combined A and B regions, where $q = q_A + q_B$:

$$S + qW \rightarrow SW_q$$

(6)

For $n_1$ moles of water and $n_2$ moles of solute, and employing standard stoichiometric techniques, one gets the following for the total volume of the solution ($V_{tot}$):

$$V_{tot} = V_1^{\cdot}[n_1 - n_2(q_A + q_B)] + n_2 V_{SW(qA+qB)}$$

(7)

Rearranging the expression and dividing both sides by $n_1$, one gets for $V^*$:

$$V^* = \frac{V_{tot}}{n_1} = V_1^{\cdot} + r\left[V_{SW(qA+qB)} - V_1^{\cdot}(q_A + q_B)\right]$$

(8)

One can sum up the volume occupied by the water-solute complex as

$$V_{SW(qA+qB)} = V_2^{int} + V_2^{void} + q_A V_{1A}^{solv} + q_B V_{1B}^{solv}$$

(9)

where $V_2^{int}$ is the intrinsic volume of the solute molecules, $V_2^{void}$ is the volume of the empty space between the solute molecules and solvated water molecules, and $q_A V_{1A}^{solv}$ and $q_B V_{1B}^{solv}$ are the volumes of solvated water around regions A and B respectively.

$V_2^{int}$ and $V_2^{void}$ can be combined into one term, $V_2^{iv}$ (the total volume taken up by one solvent molecule). The above equation is substituted into Equation 3 to get

$$V^* = V_1^{\cdot} + r[V_2^{iv} + q_A V_{1A}^{solv} - q_A V_1^{\cdot} + q_B V_{1B}^{solv} - q_B V_1^{\cdot}]$$

(10)

or

$$V^* = V_1^{\cdot} + r\left[V_2^{iv} + q_A \Delta V_{1A} + q_B \Delta V_{1B}\right],$$

(11)

where $\Delta V_{1A} = V_{1A}^{solv} - V_1^{\cdot}$.

It was determined in Equation 4 that the ideal portion of V* is equal to $V_1^{\cdot} + rV_2°$. At infinite dilution, $q_A$ and $q_B$ become $q_A°$ and $q_B°$, the solvation numbers of water around regions A and B as r approaches zero. Thus,

$$V_2° = V_2^{iv} + q_A° \Delta V_{1A} + q_B° \Delta V_{1B}$$

(12)

Combining Equations 5, 11 and 12 gives

$$V_e^* = r\left[\left(V_2^{iv} + q_A \Delta V_{1A} + q_B \Delta V_{1B}\right) - \left(V_2^{iv} + q_A° \Delta V_{1A} + q_B° \Delta V_{1B}\right)\right]$$

(13)

or

$$\frac{V_e^*}{r} = \Delta V_{1A}\left(q_A - q_A°\right) + \Delta V_{1B}\left(q_B - q_B°\right)$$

(14)

Several assumptions are made in this analysis, namely:

- $\Delta V_{1A}$ and $\Delta V_{1B}$ are functions of temperature,

- $\Delta V_{1A}$ and $\Delta V_{1B}$ are not functions of r,

- $q_A$ and $q_B$ are not functions of temperature,

- $q_A$ and $q_B$ are functions of r, and

- $\dfrac{dq_A}{dr}$ and $\dfrac{dq_B}{dr} < 0$.

## V. Relating Data to Model

Equation 2 reveals how V* may be calculated from the mole ratio r and density, $\rho$. When V* is graphed versus r and fit to a regression, the coefficients of the fit can be derived from the resulting equation of the line. For 1-butanol, 2-butanol and tert-butanol, it was found that fitting V* to either a cubic or a quartic in r gave statistically reliable coefficients. Thus, for a quartic,

$$V^* = a + br + cr^2 + er^3 + fr^4$$

(15)

where a = the molar volume of pure water, $V_1^{\cdot}$, and b = $V_2^{\circ}$, which is the partial molar volume of alcohol at infinite dilution.

The limiting linear line, or the ideal portion of V*, has been previously expressed in Equation 4 and can be alternately defined as

$$V_{ideal}^* = a + br = V_1^{\cdot} + rV_2^{\circ}$$

(16)

By subtracting this equation from Equation 16, an expression for $V_e$* can be derived:

$$V_e^* = V^* - V_{ideal}^* = cr^2 + er^3 + fr^4$$

(17)

Dividing by the mole ratio gives an expression

$$\frac{V_e^*}{r} = cr + er^2 + fr^3$$

(18)

which can be set equal to Equation 14. This equation isolates the non-linear and therefore non-ideal portion of the molar volume.

## VI. Experimental Design

Approximately 40 aqueous solutions of tert-butanol, 23 of 1-butanol and 26 of 2-butanol were prepared by the addition of varying amounts of alcohol, up to about 18 g, to about 50 to 70 g of deionized water. Each flask was shaken to give the alcohol-water solution a homogeneous distribution for measurements, and covered with parafilm when not in use to avoid evaporation. Using an Anton Paar DMA 4500 densitometer, each solution was sampled and the density measured at six temperatures: 0, 5, 10, 15, 20 and 25°C. To prevent contamination across measurements, data were collected starting from the lowest concentration up to the highest concentration solution, and the densitometer was flushed with water after each temperature measurement. Using the density and the previously determined mole ratio r, the modified volume function V* could be calculated for a given alcohol and temperature.

Several alcohols were used in our research, including methanol, ethanol, 1-propanol, 2-propanol, tert-butanol, 1-butanol and 2-butanol. I will mostly be focusing on the three butanols. The data on methanol, ethanol and 1-propanol came from the Benson lab, but data for the other alcohols were collected by us. We also took additional measurements for aqueous ethanol.

All of the analytical reagents used were manufactured by Sigma Aldrich, which is based in St. Louis, Missouri, and each had a purity of at least 95%. Additionally, when making the aqueous solutions, only deionized water was used.

## VII.    Results

Table 1 reports data for our tert-butanol solutions at all six temperatures. The comparable data for 1-butanol and 2-butanol are in the Appendix. The masses and densities were experimentally determined, and the values for V* were calculated using the molar masses, the mole ratio and the density, as per Equation 3.

Figure 1 reports V* versus r for tert-butanol at 5°C and 25°C, and is representative of all V* data at all temperatures.
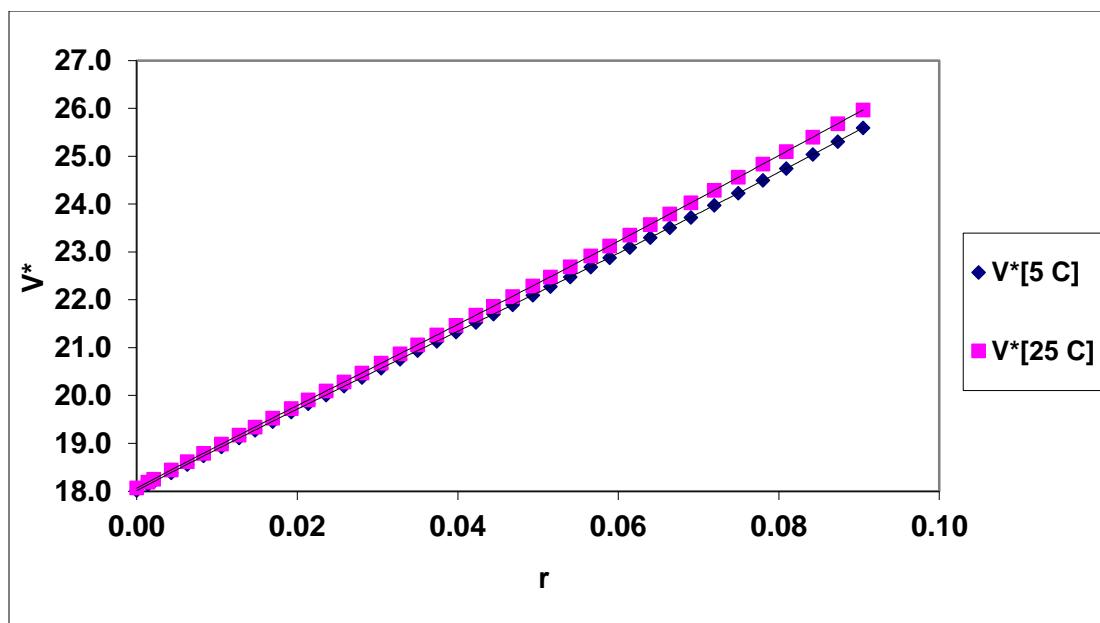


**Figure 1**. The graph of V* vs. r for tert-butanol at 5°C and 25°C.

**Table 1**. Values for solution masses, number of moles, and the mole ratio for tert-butanol, as well as densities and values of V* at all six temperatures. The molar mass of water, $M_1 = 18.015$ g/mol, and the molar mass of tert-butanol, $M_2 = 74.12$ g/mol.

| Tert- | Butanol | | | | 0°C | | 5°C | |
|---|---|---|---|---|---|---|---|---|
| $m_1$ (g) | $m_2$ (g) | $n_1$ (mol) | $n_2$ (mol) | $r$ | $\rho$ | V* | $\rho$ | V* |
| 10.0000 | 0.0000 | 0.55509 | 0.00000 | 0.00000 | 0.99990 | 18.01680 | 0.99999 | 18.01518 |
| 69.8681 | 0.4040 | 3.87833 | 0.00545 | 0.00141 | 0.99882 | 18.14057 | 0.99893 | 18.13858 |
| 69.5344 | 0.5970 | 3.85981 | 0.00805 | 0.00209 | 0.99834 | 18.19988 | 0.99845 | 18.19788 |
| 68.8621 | 1.2136 | 3.82249 | 0.01637 | 0.00428 | 0.99685 | 18.39042 | 0.99697 | 18.38821 |
| 68.2978 | 1.7684 | 3.79116 | 0.02386 | 0.00629 | 0.99562 | 18.56276 | 0.99572 | 18.56089 |
| 67.6895 | 2.3228 | 3.75740 | 0.03134 | 0.00834 | 0.99443 | 18.73756 | 0.99451 | 18.73605 |
| 67.1513 | 2.9173 | 3.72752 | 0.03936 | 0.01056 | 0.99326 | 18.92519 | 0.99331 | 18.92424 |
| 66.5697 | 3.4967 | 3.69524 | 0.04718 | 0.01277 | 0.99217 | 19.11091 | 0.99218 | 19.11072 |
| 65.9989 | 4.0065 | 3.66355 | 0.05405 | 0.01475 | 0.99126 | 19.27709 | 0.99124 | 19.27748 |
| 65.4748 | 4.5573 | 3.63446 | 0.06149 | 0.01692 | 0.99039 | 19.45588 | 0.99032 | 19.45726 |
| 64.8611 | 5.1412 | 3.60039 | 0.06936 | 0.01927 | 0.98945 | 19.65027 | 0.98933 | 19.65265 |
| 64.3871 | 5.6625 | 3.57408 | 0.07640 | 0.02138 | 0.98870 | 19.82333 | 0.98852 | 19.82694 |
| 63.8699 | 6.1994 | 3.54537 | 0.08364 | 0.02359 | 0.98796 | 20.00444 | 0.98772 | 20.00930 |
| 63.3450 | 6.7346 | 3.51624 | 0.09086 | 0.02584 | 0.98727 | 20.18727 | 0.98695 | 20.19382 |
| 62.7855 | 7.2485 | 3.48518 | 0.09779 | 0.02806 | 0.98664 | 20.36691 | 0.98625 | 20.37496 |
| 62.2535 | 7.8027 | 3.45565 | 0.10527 | 0.03046 | 0.98601 | 20.56060 | 0.98552 | 20.57082 |
| 61.7357 | 8.3312 | 3.42691 | 0.11240 | 0.03280 | 0.98542 | 20.74863 | 0.98485 | 20.76064 |
| 61.1907 | 8.8056 | 3.39665 | 0.11880 | 0.03498 | 0.98492 | 20.92295 | 0.98426 | 20.93698 |
| 60.7303 | 9.3430 | 3.37110 | 0.12605 | 0.03739 | 0.98440 | 21.11591 | 0.98363 | 21.13244 |
| 60.2285 | 9.8550 | 3.34324 | 0.13296 | 0.03977 | 0.98390 | 21.30576 | 0.98302 | 21.32483 |
| 59.7040 | 10.3834 | 3.31413 | 0.14009 | 0.04227 | 0.98342 | 21.50462 | 0.98243 | 21.52629 |
| 59.2582 | 10.8324 | 3.28938 | 0.14615 | 0.04443 | 0.98304 | 21.67576 | 0.98191 | 21.70071 |
| 58.7891 | 11.3258 | 3.26334 | 0.15280 | 0.04682 | 0.98259 | 21.86631 | 0.98135 | 21.89394 |
| 58.2580 | 11.8265 | 3.23386 | 0.15956 | 0.04934 | 0.98216 | 22.06574 | 0.98073 | 22.09791 |
| 57.7689 | 12.2482 | 3.20671 | 0.16525 | 0.05153 | 0.98176 | 22.24021 | 0.98019 | 22.27584 |
| 57.2681 | 12.7233 | 3.17891 | 0.17166 | 0.05400 | 0.98128 | 22.43744 | 0.97956 | 22.47683 |
| 56.7943 | 13.2160 | 3.15261 | 0.17831 | 0.05656 | 0.98077 | 22.64250 | 0.97889 | 22.68598 |
| 56.3235 | 13.6510 | 3.12648 | 0.18417 | 0.05891 | 0.98028 | 22.83149 | 0.97823 | 22.87934 |
| 55.8984 | 14.1318 | 3.10288 | 0.19066 | 0.06145 | 0.97973 | 23.03636 | 0.97749 | 23.08915 |
| 55.4860 | 14.6074 | 3.07999 | 0.19708 | 0.06399 | 0.97912 | 23.24299 | 0.97668 | 23.30106 |
| 54.9648 | 15.0162 | 3.05106 | 0.20259 | 0.06640 | 0.97849 | 23.44085 | 0.97588 | 23.50354 |
| 54.5536 | 15.4936 | 3.02823 | 0.20903 | 0.06903 | 0.97774 | 23.65801 | 0.97503 | 23.72377 |
| 54.0576 | 16.0032 | 3.00070 | 0.21591 | 0.07195 | 0.97685 | 23.90148 | 0.97390 | 23.97387 |
| 53.5143 | 16.5034 | 2.97054 | 0.22266 | 0.07496 | 0.97587 | 24.15351 | 0.97273 | 24.23148 |
| 53.0667 | 17.0360 | 2.94570 | 0.22984 | 0.07803 | 0.97475 | 24.41483 | 0.97149 | 24.49676 |
| 52.5108 | 17.4805 | 2.91484 | 0.23584 | 0.08091 | 0.97362 | 24.66268 | 0.97034 | 24.74604 |
| 52.0852 | 18.0524 | 2.89121 | 0.24356 | 0.08424 | 0.97232 | 24.94949 | 0.96899 | 25.03523 |
| 51.4965 | 18.5058 | 2.85853 | 0.24967 | 0.08734 | 0.97126 | 25.21351 | 0.96762 | 25.30836 |
| 51.0173 | 18.9983 | 2.83193 | 0.25632 | 0.09051 | 0.96975 | 25.49481 | 0.96605 | 25.59246 |

| | 10°C | | 15°C | | 20°C | | 25°C |
|---|---|---|---|---|---|---|---|
| $\rho$ | $V^*$ | $\rho$ | $V^*$ | $\rho$ | $V^*$ | $\rho$ | $V^*$ |
| 0.99972 | 18.02005 | 0.99911 | 18.03105 | 0.99821 | 18.04730 | 0.99706 | 18.06812 |
| 0.99867 | 18.14330 | 0.99807 | 18.15421 | 0.99717 | 18.17059 | 0.99602 | 18.19157 |
| 0.99819 | 18.20262 | 0.99760 | 18.21338 | 0.99669 | 18.23001 | 0.99554 | 18.25107 |
| 0.99671 | 18.39300 | 0.99612 | 18.40390 | 0.99520 | 18.42091 | 0.99405 | 18.44222 |
| 0.99545 | 18.56593 | 0.99484 | 18.57731 | 0.99392 | 18.59451 | 0.99276 | 18.61623 |
| 0.99423 | 18.74133 | 0.99361 | 18.75303 | 0.99266 | 18.77097 | 0.99148 | 18.79331 |
| 0.99301 | 18.92996 | 0.99236 | 18.94236 | 0.99138 | 18.96108 | 0.99018 | 18.98406 |
| 0.99186 | 19.11688 | 0.99118 | 19.13000 | 0.99017 | 19.14951 | 0.98894 | 19.17333 |
| 0.99087 | 19.28468 | 0.99016 | 19.29851 | 0.98912 | 19.31880 | 0.98785 | 19.34364 |
| 0.98991 | 19.46532 | 0.98916 | 19.48008 | 0.98807 | 19.50157 | 0.98678 | 19.52706 |
| 0.98886 | 19.66199 | 0.98806 | 19.67791 | 0.98691 | 19.70084 | 0.98557 | 19.72762 |
| 0.98800 | 19.83737 | 0.98716 | 19.85425 | 0.98596 | 19.87842 | 0.98457 | 19.90648 |
| 0.98713 | 20.02126 | 0.98622 | 20.03974 | 0.98496 | 20.06537 | 0.98352 | 20.09475 |
| 0.98630 | 20.20712 | 0.98532 | 20.22722 | 0.98402 | 20.25394 | 0.98251 | 20.28507 |
| 0.98553 | 20.38985 | 0.98449 | 20.41139 | 0.98310 | 20.44025 | 0.98154 | 20.47273 |
| 0.98472 | 20.58753 | 0.98360 | 20.61098 | 0.98212 | 20.64204 | 0.98052 | 20.67572 |
| 0.98396 | 20.77942 | 0.98276 | 20.80479 | 0.98120 | 20.83787 | 0.97951 | 20.87382 |
| 0.98329 | 20.95764 | 0.98199 | 20.98538 | 0.98035 | 21.02049 | 0.97857 | 21.05872 |
| 0.98256 | 21.15545 | 0.98119 | 21.18499 | 0.97942 | 21.22328 | 0.97755 | 21.26388 |
| 0.98184 | 21.35046 | 0.98035 | 21.38291 | 0.97851 | 21.42312 | 0.97654 | 21.46634 |
| 0.98113 | 21.55481 | 0.97953 | 21.59002 | 0.97757 | 21.63331 | 0.97549 | 21.67944 |
| 0.98051 | 21.73169 | 0.97879 | 21.76988 | 0.97669 | 21.81669 | 0.97458 | 21.86392 |
| 0.97981 | 21.92835 | 0.97798 | 21.96938 | 0.97576 | 22.01936 | 0.97350 | 22.07048 |
| 0.97904 | 22.13606 | 0.97712 | 22.17955 | 0.97446 | 22.24010 | 0.97239 | 22.28744 |
| 0.97838 | 22.31705 | 0.97630 | 22.36459 | 0.97377 | 22.42270 | 0.97138 | 22.47787 |
| 0.97758 | 22.52236 | 0.97535 | 22.57385 | 0.97271 | 22.63512 | 0.97020 | 22.69368 |
| 0.97672 | 22.73638 | 0.97435 | 22.79169 | 0.97162 | 22.85573 | 0.96893 | 22.91918 |
| 0.97592 | 22.93349 | 0.97342 | 22.99239 | 0.97056 | 23.06015 | 0.96780 | 23.12591 |
| 0.97502 | 23.14764 | 0.97238 | 23.21049 | 0.96935 | 23.28304 | 0.96654 | 23.35073 |
| 0.97407 | 23.36349 | 0.97130 | 23.43012 | 0.96818 | 23.50563 | 0.96528 | 23.57625 |
| 0.97312 | 23.57021 | 0.97020 | 23.64114 | 0.96702 | 23.71889 | 0.96406 | 23.79171 |
| 0.97204 | 23.79674 | 0.96908 | 23.86943 | 0.96526 | 23.96389 | 0.96270 | 24.02761 |
| 0.97087 | 24.04870 | 0.96772 | 24.12698 | 0.96436 | 24.21104 | 0.96131 | 24.28785 |
| 0.96954 | 24.31121 | 0.96633 | 24.39197 | 0.96301 | 24.47606 | 0.95972 | 24.55996 |
| 0.96818 | 24.58051 | 0.96493 | 24.66330 | 0.96140 | 24.75385 | 0.95819 | 24.83678 |
| 0.96688 | 24.83460 | 0.96356 | 24.92017 | 0.96011 | 25.00971 | 0.95677 | 25.09702 |
| 0.96555 | 25.12442 | 0.96202 | 25.21661 | 0.95849 | 25.30948 | 0.95513 | 25.39852 |
| 0.96404 | 25.40234 | 0.96065 | 25.49199 | 0.95696 | 25.59028 | 0.95364 | 25.67937 |
| 0.96268 | 25.68205 | 0.95902 | 25.78006 | 0.95535 | 25.87910 | 0.95205 | 25.96880 |

Graphs of V* vs. r, such as Figure 1, may be fit to polynomials, in this case a quartic regression for tert-butanol and cubic regressions for 1-butanol and 2-butanol. These fits were chosen because they yielded reliable results for the coefficients. The coefficients for each alcohol are reported in tables 2, 3, and 4.

**Table 2**. Coefficients for tert-butanol at all six temperatures.

| T (°C) | $a\ (V_1^{\bullet})$ | $b\ (V_2^{\circ})$ | $c$ | $e$ | $f$ |
|---|---|---|---|---|---|
| 0 | 18.0161 | 88.1348 | -201.0192 | 1631.3552 | -870.7083 |
| 5 | 18.0138 | 88.2616 | -201.9807 | 2041.6096 | -3986.8306 |
| 10 | 18.0178 | 88.5641 | -213.8492 | 2677.6096 | -8659.7254 |
| 15 | 18.0287 | 88.5872 | -205.3885 | 2879.9125 | -10710.0819 |
| 20 | 18.0456 | 88.5363 | -189.9906 | 3001.2027 | -12673.2559 |
| 25 | 18.0663 | 88.6273 | -179.4538 | 3072.8189 | -13831.3865 |

**Table 3**. Coefficients for 2-butanol at all six temperatures.

| T (°C) | $a\ (V_1^{\bullet})$ | $b\ (V_2^{\circ})$ | $c$ | $e$ |
|---|---|---|---|---|
| 0 | 18.0135 | 85.998 | -169.1161 | 1549.5936 |
| 5 | 18.0111 | 86.121 | -162.1206 | 1710.7063 |
| 10 | 18.0157 | 86.278 | -155.5575 | 1871.5037 |
| 15 | 18.0268 | 86.063 | -148.0629 | 2018.7897 |
| 20 | 18.0431 | 86.588 | -138.8510 | 2102.7092 |
| 25 | 18.0640 | 86.617 | -120.0166 | 2037.9684 |

**Table 4**. Coefficients for 1-butanol at all six temperatures.

| T (°C) | $a$ ($V_1^\bullet$) | $b$ ($V_2^\circ$) | $c$ | $e$ |
|---|---|---|---|---|
| 0 | 18.0173 | 85.7560 | -166.2220 | 2053.6731 |
| 5 | 18.0152 | 85.8730 | -149.4873 | 2030.0528 |
| 10 | 18.0201 | 86.0187 | -135.0793 | 2026.4922 |
| 15 | 18.0309 | 86.2636 | -128.6268 | 2263.2602 |
| 20 | 18.0473 | 86.3955 | -104.4518 | 1933.3975 |
| 25 | 18.0685 | 86.6026 | -91.1343 | 1961.3766 |

Coefficient "a" corresponds to the y-intercept of the graph, and is equivalent to $V_1^\bullet$, the molar mass of bulk water. The lowest value was at 5°C, which made sense since liquid water has a density minimum at about 4°C. Coefficient "b" corresponds to the slope of the graph, and is equivalent to $V_2^\circ$, the partial molar volume of alcohol at infinite dilution (the limit as r approaches zero). The structure of the alcohol caused little variation in $V_2^\circ$. There was a larger spread for each of the other three coefficients.

Table 5 reports the values of $V_e^*$ and $V_e^*/r$ for tert-butanol at all six temperatures. These values were calculated for each temperature by applying the coefficients from Table 2 to Equations 17 and 18.

**Table 5**. r, $V_e^*$ and $V_e^*/r$ for tert-butanol at all six temperatures.

| | 0°C | | 5°C | | 10°C | |
|---|---|---|---|---|---|---|
| $r$ | $V_e^*$ | $V_e^*/r$ | $V_e^*$ | $V_e^*/r$ | $V_e^*$ | $V_e^*/r$ |
| 0.00000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.00141 | -0.000393 | -0.27929 | -0.000393 | -0.2798 | -0.000415 | -0.2953 |
| 0.00209 | -0.000861 | -0.41238 | -0.000861 | -0.4126 | -0.000907 | -0.4347 |
| 0.00428 | -0.00356 | -0.83112 | -0.003547 | -0.8280 | -0.003716 | -0.8676 |
| 0.00629 | -0.007556 | -1.20045 | -0.007497 | -1.1912 | -0.007816 | -1.2419 |
| 0.00834 | -0.013041 | -1.56311 | -0.012885 | -1.5449 | -0.013364 | -1.6024 |
| 0.01056 | -0.020503 | -1.94069 | -0.020166 | -1.9098 | -0.020798 | -1.9697 |
| 0.01277 | -0.029393 | -2.30047 | -0.028778 | -2.2542 | -0.029514 | -2.3118 |
| 0.01475 | -0.038563 | -2.61081 | -0.037602 | -2.5485 | -0.038364 | -2.6002 |
| 0.01692 | -0.049704 | -2.93382 | -0.048248 | -2.8520 | -0.048948 | -2.8934 |
| 0.01927 | -0.063065 | -3.26723 | -0.060917 | -3.1620 | -0.061418 | -3.1880 |
| 0.02138 | -0.076094 | -3.55145 | -0.073178 | -3.4235 | -0.073364 | -3.4322 |
| 0.02359 | -0.090728 | -3.83438 | -0.086842 | -3.6811 | -0.086544 | -3.6685 |
| 0.02584 | -0.106466 | -4.10511 | -0.101418 | -3.9248 | -0.100453 | -3.8875 |
| 0.02806 | -0.122773 | -4.35613 | -0.116398 | -4.1482 | -0.114588 | -4.0837 |
| 0.03046 | -0.141181 | -4.60981 | -0.133159 | -4.3711 | -0.130217 | -4.2745 |
| 0.03280 | -0.159703 | -4.83833 | -0.149868 | -4.5692 | -0.145602 | -4.4391 |
| 0.03498 | -0.177415 | -5.03519 | -0.165701 | -4.7375 | -0.160000 | -4.5745 |
| 0.03739 | -0.197473 | -5.23562 | -0.183461 | -4.9064 | -0.175939 | -4.7053 |
| 0.03977 | -0.217503 | -5.41428 | -0.201013 | -5.0544 | -0.191469 | -4.8144 |
| 0.04227 | -0.238744 | -5.58227 | -0.219425 | -5.1910 | -0.207514 | -4.9092 |
| 0.04443 | -0.257129 | -5.71094 | -0.235189 | -5.2935 | -0.221046 | -4.9752 |
| 0.04682 | -0.277443 | -5.83581 | -0.252413 | -5.3906 | -0.235604 | -5.0317 |
| 0.04934 | -0.298579 | -5.94686 | -0.270109 | -5.4744 | -0.250303 | -5.0730 |
| 0.05153 | -0.316712 | -6.02678 | -0.285099 | -5.5325 | -0.262535 | -5.0946 |
| 0.05400 | -0.336688 | -6.09798 | -0.301390 | -5.5814 | -0.275586 | -5.1035 |
| 0.05656 | -0.356789 | -6.15085 | -0.317528 | -5.6142 | -0.288244 | -5.0964 |
| 0.05891 | -0.374571 | -6.18059 | -0.331567 | -5.6286 | -0.299013 | -5.0759 |
| 0.06145 | -0.392918 | -6.19246 | -0.345791 | -5.6275 | -0.309664 | -5.0396 |
| 0.06399 | -0.410244 | -6.18330 | -0.358938 | -5.6096 | -0.319245 | -4.9893 |
| 0.06640 | -0.42563 | -6.15508 | -0.370337 | -5.5773 | -0.327308 | -4.9293 |
| 0.06903 | -0.441032 | -6.10276 | -0.381425 | -5.5256 | -0.334883 | -4.8514 |
| 0.07195 | -0.456353 | -6.01803 | -0.392028 | -5.4484 | -0.341804 | -4.7504 |
| 0.07496 | -0.469872 | -5.90202 | -0.400868 | -5.3481 | -0.347217 | -4.6323 |
| 0.07803 | -0.481154 | -5.75289 | -0.407622 | -5.2241 | -0.350959 | -4.4979 |
| 0.08091 | -0.489191 | -5.58489 | -0.411729 | -5.0887 | -0.352814 | -4.3606 |
| 0.08424 | -0.495134 | -5.35713 | -0.413631 | -4.9101 | -0.352974 | -4.1901 |
| 0.08734 | -0.497201 | -5.11232 | -0.412528 | -4.7231 | -0.351245 | -4.0214 |
| 0.09051 | -0.495604 | -4.8301 | -0.408415 | -4.5124 | -0.347669 | -3.8412 |

| | 15°C | | 20°C | | 25°C | |
|---|---|---|---|---|---|---|
| $r$ | $V_e*$ | $V_e*/r$ | $V_e*$ | $V_e*/r$ | $V_e*$ | $V_e*/r$ |
| 0.00000 | 0 | 0 | 0 | 0 | 0 | 0.0000 |
| 0.00141 | -0.0004 | -0.2830 | -0.0004 | -0.2611 | -0.0003 | -0.2462 |
| 0.00209 | -0.0009 | -0.4162 | -0.0008 | -0.3835 | -0.0008 | -0.3612 |
| 0.00428 | -0.0035 | -0.8278 | -0.0033 | -0.7597 | -0.0031 | -0.7134 |
| 0.00629 | -0.0074 | -1.1812 | -0.0068 | -1.0799 | -0.0064 | -1.0111 |
| 0.00834 | -0.0127 | -1.5189 | -0.0115 | -1.3832 | -0.0108 | -1.2910 |
| 0.01056 | -0.0196 | -1.8602 | -0.0178 | -1.6864 | -0.0166 | -1.5685 |
| 0.01277 | -0.0278 | -2.1750 | -0.0251 | -1.9628 | -0.0232 | -1.8190 |
| 0.01475 | -0.036 | -2.4379 | -0.0323 | -2.1906 | -0.0299 | -2.0232 |
| 0.01692 | -0.0457 | -2.7023 | -0.0409 | -2.4166 | -0.0376 | -2.2234 |
| 0.01927 | -0.0571 | -2.9646 | -0.0508 | -2.637 | -0.0465 | -2.4157 |
| 0.02138 | -0.0680 | -3.1790 | -0.0601 | -2.8136 | -0.0549 | -2.5670 |
| 0.02359 | -0.0798 | -3.3832 | -0.0703 | -2.9782 | -0.0638 | -2.7050 |
| 0.02584 | -0.0922 | -3.5691 | -0.0807 | -3.1241 | -0.0730 | -2.8240 |
| 0.02806 | -0.1047 | -3.7323 | -0.0911 | -3.2481 | -0.0820 | -2.9216 |
| 0.03046 | -0.1184 | -3.8870 | -0.1024 | -3.3609 | -0.0916 | -3.0062 |
| 0.03280 | -0.1317 | -4.0163 | -0.1132 | -3.4501 | -0.1006 | -3.0683 |
| 0.03498 | -0.1441 | -4.1189 | -0.1230 | -3.5159 | -0.1088 | -3.1093 |
| 0.03739 | -0.1575 | -4.2132 | -0.1335 | -3.5705 | -0.1173 | -3.1369 |
| 0.03977 | -0.1705 | -4.2870 | -0.1434 | -3.6062 | -0.1251 | -3.1468 |
| 0.04227 | -0.1837 | -4.3450 | -0.1533 | -3.6257 | -0.1327 | -3.1398 |
| 0.04443 | -0.1946 | -4.3797 | -0.1612 | -3.6284 | -0.1386 | -3.1204 |
| 0.04682 | -0.2061 | -4.4024 | -0.1694 | -3.6171 | -0.1445 | -3.0856 |
| 0.04934 | -0.2176 | -4.4093 | -0.1771 | -3.5901 | -0.1497 | -3.0350 |
| 0.05153 | -0.2268 | -4.4020 | -0.1832 | -3.5550 | -0.1536 | -2.9804 |
| 0.05400 | -0.2365 | -4.3796 | -0.1892 | -3.5036 | -0.1570 | -2.9081 |
| 0.05656 | -0.2456 | -4.3417 | -0.1944 | -3.4380 | -0.1596 | -2.8225 |
| 0.05891 | -0.2530 | -4.2946 | -0.1984 | -3.3680 | -0.1611 | -2.7355 |
| 0.06145 | -0.2600 | -4.2316 | -0.2017 | -3.2829 | -0.1618 | -2.6338 |
| 0.06399 | -0.2660 | -4.1568 | -0.2041 | -3.1892 | -0.1616 | -2.5252 |
| 0.06640 | -0.2706 | -4.0758 | -0.2054 | -3.0933 | -0.1605 | -2.4170 |
| 0.06903 | -0.2746 | -3.9778 | -0.2059 | -2.9827 | -0.1584 | -2.2950 |
| 0.07195 | -0.2776 | -3.8580 | -0.2053 | -2.8535 | -0.1551 | -2.1560 |
| 0.07496 | -0.2792 | -3.7250 | -0.2036 | -2.7161 | -0.1508 | -2.0117 |
| 0.07803 | -0.2793 | -3.5801 | -0.2007 | -2.5728 | -0.1455 | -1.8648 |
| 0.08091 | -0.2781 | -3.4377 | -0.1972 | -2.4376 | -0.1400 | -1.7297 |
| 0.08424 | -0.2753 | -3.2674 | -0.1923 | -2.2832 | -0.1331 | -1.5797 |
| 0.08734 | -0.2712 | -3.1053 | -0.1872 | -2.1432 | -0.1265 | -1.4483 |
| 0.09051 | -0.2660 | -2.9384 | -0.1816 | -2.0068 | -0.1199 | -1.3251 |

Figures 2, 3 and 4 report $V_e^*/r$ versus r at all temperatures for 1-butanol, 2-butanol, and tert-butanol, respectively.
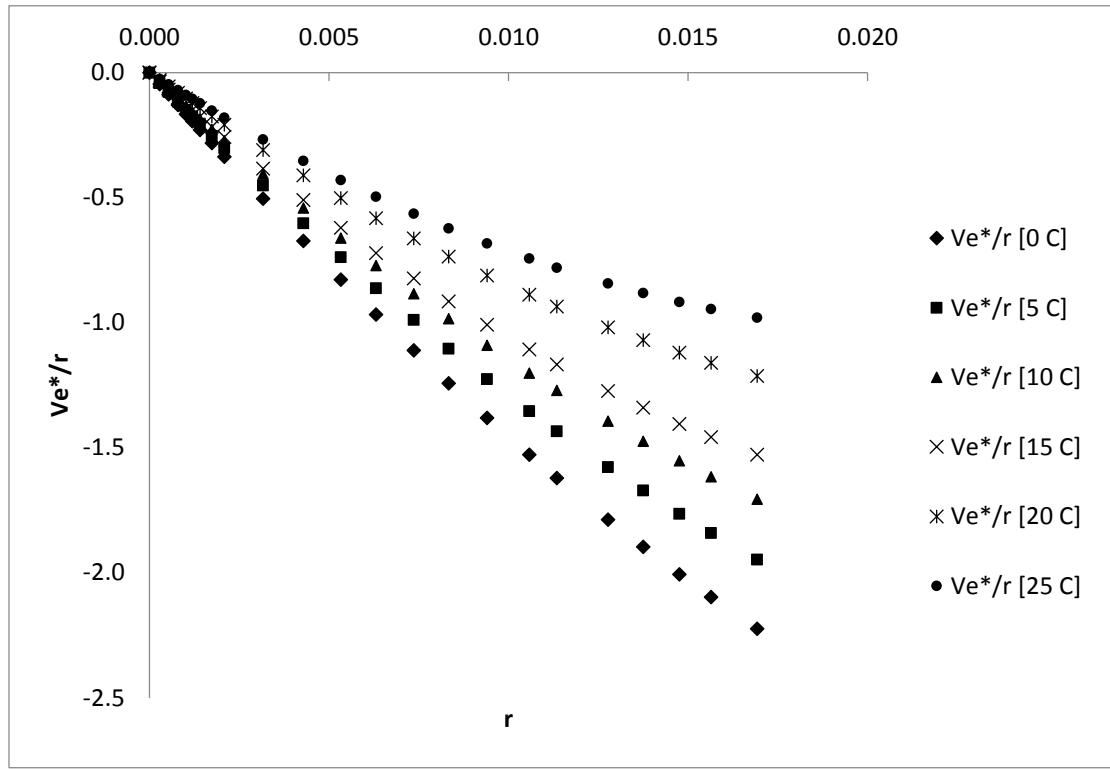


**Figure 2**. The graph of $V_e^*/r$ vs. r for 1-butanol at all six temperatures.
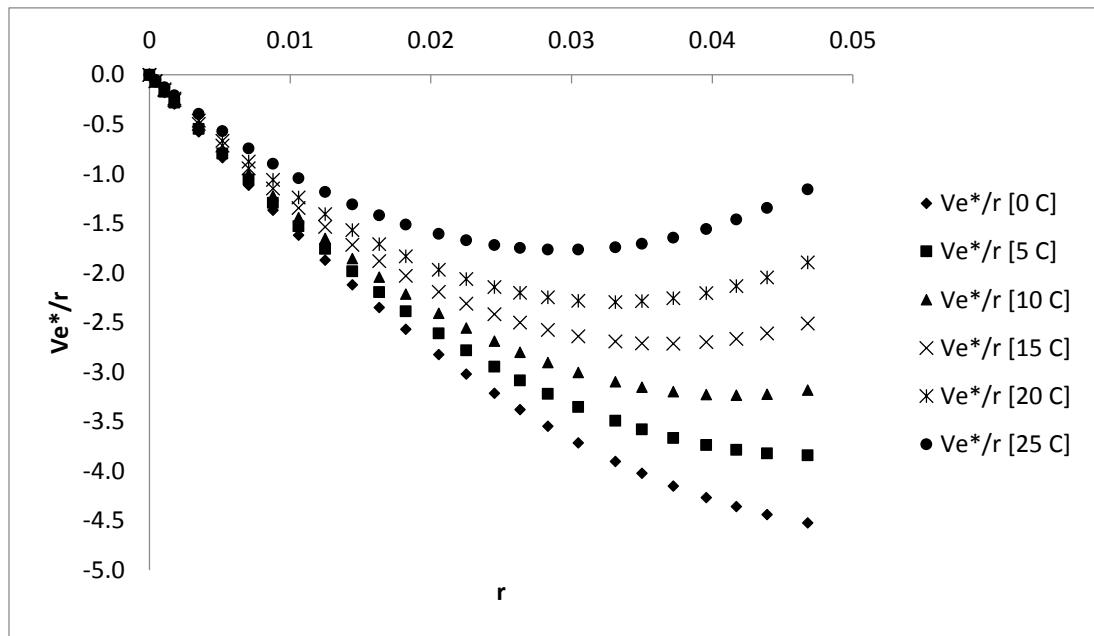


**Figure 3**. The graph of $V_e^*/r$ vs. r for 2-butanol at all six temperatures.
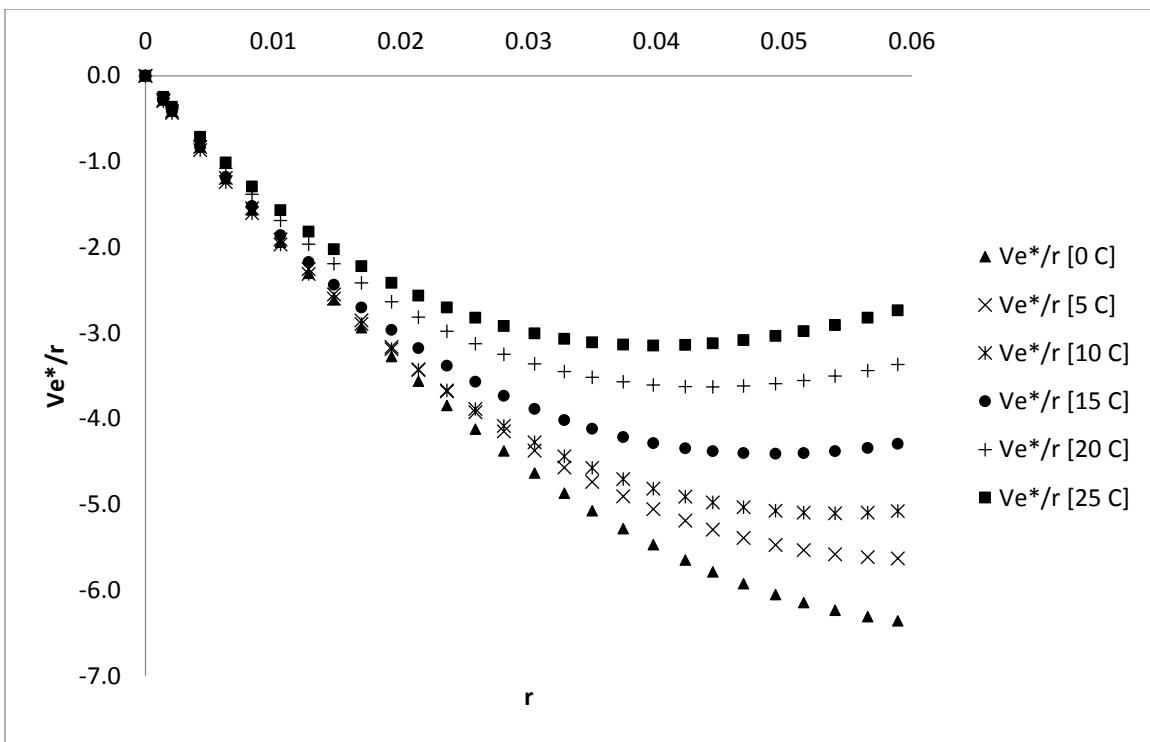
**Figure 4**. The graph of $V_e*/r$ vs. r for tert-butanol at all six temperatures. As temperature decreases, the concentration curve becomes steeper.
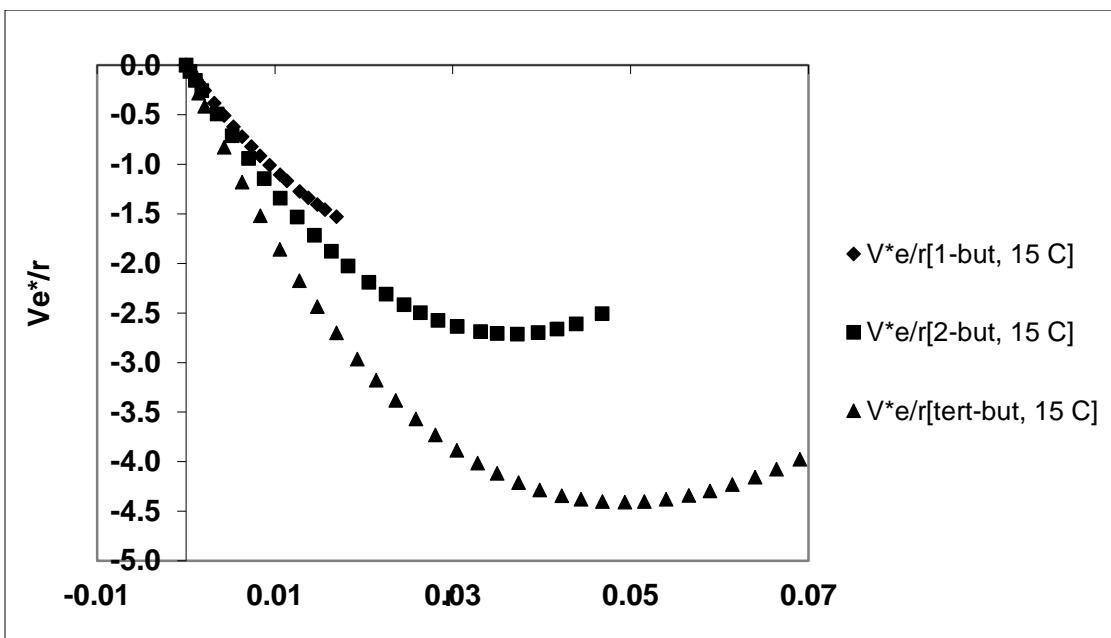


**Figure 6**. The graph of $V_e*/r$ vs. r for all three butanols at 15°C. The concentration curve becomes steeper as the alcohol group is shifted from a primary carbon to a secondary position to a tertiary position. The rest of our data is consistent with this graph.

## VIII. Discussion

We found that for a given alcohol as a function of temperature, as temperature increases, $V_e^*/r$ gets less negative at a given r. In addition, as temperature increases, $r_{min}$ decreases. For different isomers, we noticed a trend when going from primary to secondary to tertiary alcohols. $V_e^*/r$ gets more negative at a given r, and $r_{min}$ increases. This was found to be the case for the three butanols, and these results are corroborated in my colleague's work on 1- and 2-propanol.

From equation 14, we know that

$$\frac{V_e^*}{r} = \Delta V_{1A}\left(q_A - q_A^\circ\right) + \Delta V_{1B}\left(q_B - q_B^\circ\right).$$

As r increases, the solvation spheres around each alcohol molecule begin to overlap. As a consequence, $q_A^\circ$ and $q_B^\circ$ will always be the maximum values of $q_A$ and $q_B$, making the q terms in equation 14 negative. $\Delta V_{1A}$ is a positive term, since the hydrocarbon chain acts as a solvent structure maker, and $\Delta V_{1B}$ is negative because the alcohol acts as a solvent structure breaker. We find that $V_e^*/r = (+)(-) + (-)(-)$, which simplifies to $(-) + (+)$. The first term is negative, and the second term is positive. At low r, the first term predominates, resulting in the initial negative slope of the $V_e^*/r$ versus r graph as seen for tert-butanol in Figure 4. At higher r, the presence of more hydrophilic moieties causes the second term to become larger, partially canceling out the first term and giving the graph a positive slope. As temperature is increased, the initial slope of the graph becomes more steeply negative, and thus the absolute value of $\Delta V_{1A}$ can be seen to increase. However, the reason for this is unknown and we must defer to a more detailed analysis of the temperature effect.

Secondly, if we assume that $\Delta V_{1B}$, $\Delta V_{1A}$ and $(q_B-q_B^\circ)$ are independent of isomer, then we conclude that $|(q_A-q_A^\circ)|$ increases as we go from a primary to a secondary to a tertiary alcohol. The reason for this is unknown and requires further study, though it may have to do with the sterics of the solute molecules. Future work might be done to construct a molecular model for our system in order to confirm our results, but this will require further research to be done at a later date.

## IX.    Acknowledgments

First, I would like to thank Dr. Anthony Fucaloro for his invaluable guidance and insight throughout the entirety of my thesis research. I would also like to thank Dr. Mary Hatcher-Skeers for agreeing to be my second thesis reader, as well as Allison Hu (CMC '15), Alyssa Yoshino (CMC '16), and the other people I worked with in the lab over this past summer.

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## XI.  Appendix

The following tables contain the raw data collected during our temperature dependence experiments for 1-butanol, 2-butanol and tert-butanol at all six temperatures.

The molar mass for all three butanols is 74.12 g/mol.

**Table 6**. Masses, densities and calculated values of V* for 1-butanol at all temperatures.

| | | 1-Butanol | | | | 0°C | | 5°C |
|---|---|---|---|---|---|---|---|---|
| $m_1$ (g) | $m_2$ (g) | $n_1$ (mol) | $n_2$ (mol) | $r$ | $\rho$ | $V^*$ | $\rho$ | $V^*$ |
| 10.0116 | 0.0000 | 0.55574 | 0.00000 | 0.00000 | 0.99987 | 18.01734 | 0.99999 | 18.01518 |
| 71.1077 | 0.0832 | 3.94714 | 0.00112 | 0.00028 | 0.99968 | 18.04185 | 0.99980 | 18.03969 |
| 70.8977 | 0.1556 | 3.93548 | 0.00210 | 0.00053 | 0.99953 | 18.06303 | 0.99964 | 18.06104 |
| 70.6065 | 0.2286 | 3.91932 | 0.00308 | 0.00079 | 0.99937 | 18.08472 | 0.99948 | 18.08273 |
| 70.3746 | 0.2945 | 3.90644 | 0.00397 | 0.00102 | 0.99922 | 18.10451 | 0.99934 | 18.10234 |
| 70.1022 | 0.3443 | 3.89132 | 0.00465 | 0.00119 | 0.99912 | 18.11942 | 0.99923 | 18.11743 |
| 69.8695 | 0.4031 | 3.87841 | 0.00544 | 0.00140 | 0.99900 | 18.13707 | 0.99911 | 18.13507 |
| 69.7066 | 0.4982 | 3.86936 | 0.00672 | 0.00174 | 0.99880 | 18.16555 | 0.99890 | 18.16374 |
| 69.5385 | 0.5961 | 3.86003 | 0.00804 | 0.00208 | 0.99857 | 18.19545 | 0.99868 | 18.19344 |
| 69.2057 | 0.8993 | 3.84156 | 0.01213 | 0.00316 | 0.99795 | 18.28659 | 0.99804 | 18.28494 |
| 68.8666 | 1.2130 | 3.82274 | 0.01637 | 0.00428 | 0.99732 | 18.38157 | 0.99740 | 18.38010 |
| 68.5015 | 1.5025 | 3.80247 | 0.02027 | 0.00533 | 0.99675 | 18.47017 | 0.99681 | 18.46905 |
| 68.2950 | 1.7732 | 3.79101 | 0.02392 | 0.00631 | 0.99624 | 18.55250 | 0.99628 | 18.55175 |
| 67.9087 | 2.0551 | 3.76956 | 0.02773 | 0.00736 | 0.99573 | 18.63977 | 0.99575 | 18.63940 |
| 67.6818 | 2.3205 | 3.75697 | 0.03131 | 0.00833 | 0.99525 | 18.72158 | 0.99524 | 18.72177 |
| 67.4050 | 2.6071 | 3.74160 | 0.03517 | 0.00940 | 0.99475 | 18.81054 | 0.99473 | 18.81092 |
| 67.1576 | 2.9219 | 3.72787 | 0.03942 | 0.01057 | 0.99422 | 18.90809 | 0.99417 | 18.90904 |
| 66.8081 | 3.1175 | 3.70847 | 0.04206 | 0.01134 | 0.99388 | 18.97175 | 0.99382 | 18.97290 |
| 66.5775 | 3.4974 | 3.69567 | 0.04719 | 0.01277 | 0.99330 | 19.08925 | 0.99320 | 19.09117 |
| 66.3038 | 3.7498 | 3.68048 | 0.05059 | 0.01375 | 0.99290 | 19.16994 | 0.99277 | 19.17245 |
| 65.9907 | 4.0073 | 3.66310 | 0.05407 | 0.01476 | 0.99249 | 19.25356 | 0.99233 | 19.25666 |
| 65.7721 | 4.2308 | 3.65096 | 0.05708 | 0.01563 | 0.99217 | 19.32513 | 0.99198 | 19.32883 |
| 65.4642 | 4.5570 | 3.63387 | 0.06148 | 0.01692 | 0.99168 | 19.43070 | 0.99145 | 19.43521 |

| | 10°C | | 15°C | | 20°C | | 25°C |
|---|---|---|---|---|---|---|---|
| $\rho$ | $V*$ | $\rho$ | $V*$ | $P$ | $V*$ | $\rho$ | $V*$ |
| 0.99971 | 18.02023 | 0.99912 | 18.03087 | 0.99821 | 18.04730 | 0.99706 | 18.06812 |
| 0.99953 | 18.04456 | 0.99892 | 18.05558 | 0.99802 | 18.07186 | 0.99686 | 18.09289 |
| 0.99936 | 18.06610 | 0.99876 | 18.07695 | 0.99785 | 18.09344 | 0.99669 | 18.11450 |
| 0.99920 | 18.08780 | 0.99860 | 18.09866 | 0.99768 | 18.11535 | 0.99652 | 18.13644 |
| 0.99905 | 18.10759 | 0.99845 | 18.11847 | 0.99754 | 18.13500 | 0.99625 | 18.15848 |
| 0.99894 | 18.12269 | 0.99833 | 18.13376 | 0.99742 | 18.15031 | 0.99625 | 18.17162 |
| 0.99882 | 18.14034 | 0.99821 | 18.15143 | 0.99730 | 18.16799 | 0.99613 | 18.18933 |
| 0.99862 | 18.16883 | 0.99800 | 18.18012 | 0.99708 | 18.19689 | 0.99591 | 18.21827 |
| 0.99838 | 18.19891 | 0.99777 | 18.21004 | 0.99685 | 18.22684 | 0.99567 | 18.24844 |
| 0.99773 | 18.29062 | 0.99710 | 18.30217 | 0.99617 | 18.31926 | 0.99499 | 18.34099 |
| 0.99708 | 18.38600 | 0.99643 | 18.39799 | 0.99549 | 18.41537 | 0.99429 | 18.43759 |
| 0.99648 | 18.47517 | 0.99582 | 18.48742 | 0.99487 | 18.50507 | 0.99365 | 18.52779 |
| 0.99593 | 18.55827 | 0.99526 | 18.57076 | 0.99429 | 18.58888 | 0.99306 | 18.61191 |
| 0.99539 | 18.64614 | 0.99469 | 18.65926 | 0.99370 | 18.67785 | 0.99246 | 18.70119 |
| 0.99486 | 18.72892 | 0.99415 | 18.74229 | 0.99315 | 18.76117 | 0.99189 | 18.78500 |
| 0.99433 | 18.81849 | 0.99360 | 18.83231 | 0.99257 | 18.85186 | 0.99129 | 18.87620 |
| 0.99374 | 18.91722 | 0.99299 | 18.93151 | 0.99194 | 18.95155 | 0.99062 | 18.97680 |
| 0.99337 | 18.98149 | 0.99261 | 18.99602 | 0.99153 | 19.01671 | 0.99021 | 19.04206 |
| 0.99272 | 19.10040 | 0.99192 | 19.11581 | 0.99081 | 19.13722 | 0.98947 | 19.16314 |
| 0.99227 | 19.18211 | 0.99144 | 19.19817 | 0.99031 | 19.22008 | 0.98895 | 19.24651 |
| 0.99180 | 19.26695 | 0.99095 | 19.28348 | 0.98980 | 19.30588 | 0.98840 | 19.33323 |
| 0.99143 | 19.33956 | 0.99056 | 19.35654 | 0.98938 | 19.37963 | 0.98796 | 19.40748 |
| 0.99086 | 19.44678 | 0.98995 | 19.46465 | 0.98873 | 19.48867 | 0.98728 | 19.51729 |

**Table 7.** Masses, densities and calculated V* values for 2-butanol at all temperatures.

| 2-Butanol | | | | | 0°C | | 5°C | |
|---|---|---|---|---|---|---|---|---|
| $m_1$ (g) | $m_2$ (g) | $n_1$ (mol) | $n_2$ (mol) | $r$ | $\rho$ | V* | $\rho$ | V* |
| 10.0000 | 0.0000 | 0.55509 | 0.00000 | 0.00000 | 0.99986 | 18.01752 | 0.99999 | 18.01518 |
| 71.9491 | 0.1283 | 3.99384 | 0.00173 | 0.00043 | 0.99989 | 18.04911 | 1.00001 | 18.04694 |
| 71.7467 | 0.3143 | 3.98261 | 0.00424 | 0.00106 | 0.99947 | 18.10351 | 0.99959 | 18.10134 |
| 71.5205 | 0.5217 | 3.97005 | 0.00704 | 0.00177 | 0.99897 | 18.16512 | 0.99909 | 18.16293 |
| 70.9876 | 1.0221 | 3.94047 | 0.01379 | 0.00350 | 0.99797 | 18.31155 | 0.99808 | 18.30953 |
| 70.5778 | 1.5056 | 3.91772 | 0.02031 | 0.00518 | 0.99697 | 18.45521 | 0.99706 | 18.45355 |
| 69.9530 | 2.0264 | 3.88304 | 0.02734 | 0.00704 | 0.99604 | 18.61054 | 0.99611 | 18.60923 |
| 69.5722 | 2.5146 | 3.86190 | 0.03393 | 0.00878 | 0.99516 | 18.75690 | 0.99521 | 18.75595 |
| 68.9674 | 3.0091 | 3.82833 | 0.04060 | 0.01060 | 0.99436 | 18.90763 | 0.99437 | 18.90744 |
| 68.5587 | 3.5221 | 3.80565 | 0.04752 | 0.01249 | 0.99351 | 19.06420 | 0.99349 | 19.06458 |
| 67.9544 | 4.0341 | 3.77210 | 0.05443 | 0.01443 | 0.99278 | 19.22322 | 0.99272 | 19.22438 |
| 67.6138 | 4.5434 | 3.75319 | 0.06130 | 0.01633 | 0.99203 | 19.37997 | 0.99192 | 19.38212 |
| 66.9853 | 5.0237 | 3.71831 | 0.06778 | 0.01823 | 0.99138 | 19.53442 | 0.99122 | 19.53758 |
| 66.4918 | 5.6233 | 3.69091 | 0.07587 | 0.02055 | 0.99063 | 19.72332 | 0.99040 | 19.72790 |
| 66.2042 | 6.1309 | 3.67495 | 0.08271 | 0.02251 | 0.99003 | 19.88147 | 0.98973 | 19.88749 |
| 65.4986 | 6.6057 | 3.63578 | 0.08912 | 0.02451 | 0.98945 | 20.04327 | 0.98909 | 20.05056 |
| 64.9236 | 7.0368 | 3.60386 | 0.09494 | 0.02634 | 0.98897 | 20.19022 | 0.98853 | 20.19920 |
| 64.6425 | 7.5326 | 3.58826 | 0.10162 | 0.02832 | 0.98846 | 20.34901 | 0.98795 | 20.35951 |
| 64.0095 | 8.0270 | 3.55312 | 0.10829 | 0.03048 | 0.98795 | 20.52136 | 0.98736 | 20.53362 |
| 63.5218 | 8.6530 | 3.52605 | 0.11674 | 0.03311 | 0.98733 | 20.73162 | 0.98661 | 20.74675 |
| 62.9564 | 9.0683 | 3.49467 | 0.12234 | 0.03501 | 0.98691 | 20.88319 | 0.98609 | 20.90055 |
| 62.5005 | 9.5781 | 3.46936 | 0.12922 | 0.03725 | 0.98644 | 21.06129 | 0.98551 | 21.08116 |
| 62.0357 | 10.1040 | 3.44356 | 0.13632 | 0.03959 | 0.98595 | 21.24762 | 0.98488 | 21.27071 |
| 61.6159 | 10.5783 | 3.42026 | 0.14271 | 0.04173 | 0.98545 | 21.41941 | 0.98424 | 21.44574 |
| 60.9805 | 11.0124 | 3.38498 | 0.14857 | 0.04389 | 0.98495 | 21.59320 | 0.98358 | 21.62328 |
| 60.5943 | 11.6638 | 3.36355 | 0.15736 | 0.04678 | 0.98425 | 21.82638 | 0.98265 | 21.86192 |

|  | 10°C |  | 15°C |  | 20°C |  | 25°C |
| --- | --- | --- | --- | --- | --- | --- | --- |
| $\rho$ | $V*$ | $\rho$ | $V*$ | $\rho$ | $V*$ | $\rho$ | $V*$ |
| 0.99972 | 18.02005 | 0.99911 | 18.03105 | 0.99821 | 18.04730 | 0.99706 | 18.06812 |
| 0.99974 | 18.05182 | 0.99912 | 18.06302 | 0.99822 | 18.07930 | 0.99706 | 18.10034 |
| 0.99932 | 18.10623 | 0.99870 | 18.11747 | 0.99779 | 18.13399 | 0.99664 | 18.15492 |
| 0.99882 | 18.16784 | 0.99819 | 18.17931 | 0.99728 | 18.19590 | 0.99613 | 18.21690 |
| 0.99781 | 18.31449 | 0.99717 | 18.32624 | 0.99625 | 18.34317 | 0.99509 | 18.36455 |
| 0.99677 | 18.45892 | 0.99612 | 18.47096 | 0.99519 | 18.48822 | 0.99402 | 18.50998 |
| 0.99579 | 18.61521 | 0.99512 | 18.62775 | 0.99416 | 18.64574 | 0.99298 | 18.66789 |
| 0.99487 | 18.76236 | 0.99418 | 18.77538 | 0.99320 | 18.79391 | 0.99199 | 18.81683 |
| 0.99400 | 18.91447 | 0.99329 | 18.92799 | 0.99228 | 18.94726 | 0.99106 | 18.97058 |
| 0.99308 | 19.07245 | 0.99233 | 19.08686 | 0.99128 | 19.10708 | 0.99003 | 19.13121 |
| 0.99226 | 19.23329 | 0.99148 | 19.24842 | 0.99039 | 19.26961 | 0.98911 | 19.29455 |
| 0.99142 | 19.39189 | 0.99059 | 19.40814 | 0.98946 | 19.43030 | 0.98815 | 19.45606 |
| 0.99068 | 19.54822 | 0.98980 | 19.56560 | 0.98863 | 19.58876 | 0.98726 | 19.61594 |
| 0.98979 | 19.74006 | 0.98885 | 19.75882 | 0.98761 | 19.78363 | 0.98619 | 19.81212 |
| 0.98907 | 19.90077 | 0.98807 | 19.92091 | 0.98679 | 19.94675 | 0.98531 | 19.97671 |
| 0.98835 | 20.06557 | 0.98730 | 20.08691 | 0.98595 | 20.11442 | 0.98441 | 20.14588 |
| 0.98773 | 20.21556 | 0.98661 | 20.23851 | 0.98520 | 20.26748 | 0.98362 | 20.30003 |
| 0.98707 | 20.37766 | 0.98588 | 20.40226 | 0.98441 | 20.43272 | 0.98275 | 20.46724 |
| 0.98640 | 20.55361 | 0.98512 | 20.58031 | 0.98356 | 20.61296 | 0.98182 | 20.64949 |
| 0.98553 | 20.76949 | 0.98414 | 20.79882 | 0.98246 | 20.83439 | 0.98061 | 20.87370 |
| 0.98492 | 20.92538 | 0.98343 | 20.95709 | 0.98165 | 20.99509 | 0.97975 | 21.03580 |
| 0.98422 | 21.10879 | 0.98261 | 21.14338 | 0.98070 | 21.18456 | 0.97867 | 21.22850 |
| 0.98345 | 21.30164 | 0.98170 | 21.33961 | 0.97968 | 21.38361 | 0.97757 | 21.42976 |
| 0.98267 | 21.48000 | 0.98078 | 21.52140 | 0.97862 | 21.56890 | 0.97640 | 21.61794 |
| 0.98187 | 21.66093 | 0.97984 | 21.70581 | 0.97757 | 21.75621 | 0.97525 | 21.80797 |
| 0.98072 | 21.90494 | 0.97852 | 21.95419 | 0.97612 | 22.00817 | 0.97373 | 22.06219 |

**Table 8**. Calculated values of $V_e^*$ and $V_e^*/r$ for 1-butanol at all temperatures.

| | 0°C | | 5°C | | 10°C | |
|---|---|---|---|---|---|---|
| $r$ | $V_e^*$ | $V_e^*/r$ | $V_e^*$ | $V_e^*/r$ | $V_e^*$ | $V_e^*/r$ |
| 0.00000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| 0.00028 | -0.000013 | -0.047105 | -0.000012 | -0.042348 | -0.000011 | -0.038251 |
| 0.00053 | -0.000047 | -0.088083 | -0.000042 | -0.079163 | -0.000038 | -0.071479 |
| 0.00079 | -0.000102 | -0.129532 | -0.000092 | -0.116377 | -0.000083 | -0.105042 |
| 0.00102 | -0.000170 | -0.166942 | -0.000153 | -0.149945 | -0.000138 | -0.135294 |
| 0.00119 | -0.000233 | -0.195497 | -0.000210 | -0.175554 | -0.000189 | -0.158360 |
| 0.00140 | -0.000321 | -0.229046 | -0.000288 | -0.205626 | -0.000260 | -0.185430 |
| 0.00174 | -0.000491 | -0.282550 | -0.000440 | -0.253551 | -0.000397 | -0.228533 |
| 0.00208 | -0.000703 | -0.337408 | -0.000631 | -0.302644 | -0.000568 | -0.272640 |
| 0.00316 | -0.001593 | -0.504503 | -0.001427 | -0.451884 | -0.001284 | -0.406414 |
| 0.00428 | -0.002885 | -0.673967 | -0.002580 | -0.602758 | -0.002317 | -0.541142 |
| 0.00533 | -0.004413 | -0.827773 | -0.003941 | -0.739231 | -0.003532 | -0.662522 |
| 0.00631 | -0.006103 | -0.967170 | -0.005443 | -0.862505 | -0.004870 | -0.771724 |
| 0.00736 | -0.008176 | -1.111522 | -0.007280 | -0.989709 | -0.006502 | -0.883925 |
| 0.00833 | -0.010354 | -1.242541 | -0.009206 | -1.104729 | -0.008207 | -0.984912 |
| 0.00940 | -0.012984 | -1.381125 | -0.011524 | -1.225893 | -0.010254 | -1.090761 |
| 0.01057 | -0.016159 | -1.528100 | -0.014316 | -1.353777 | -0.012709 | -1.201814 |
| 0.01134 | -0.018386 | -1.621061 | -0.016267 | -1.434301 | -0.014419 | -1.271348 |
| 0.01277 | -0.022823 | -1.787508 | -0.020144 | -1.577693 | -0.017802 | -1.394315 |
| 0.01375 | -0.026073 | -1.896814 | -0.022973 | -1.671246 | -0.020259 | -1.473870 |
| 0.01476 | -0.029607 | -2.005962 | -0.026037 | -1.764114 | -0.022910 | -1.552237 |
| 0.01563 | -0.032782 | -2.096787 | -0.028782 | -1.840924 | -0.025273 | -1.616535 |
| 0.01692 | -0.037635 | -2.224438 | -0.032959 | -1.948066 | -0.028852 | -1.705316 |

|  | 15°C | | 20°C | | 25°C | |
|---|---|---|---|---|---|---|
| $r$ | $V_e^*$ | $V_e^*/r$ | $V_e^*$ | $V_e^*/r$ | $V_e^*$ | $V_e^*/r$ |
| 0.00000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| 0.00028 | -0.000010 | -0.036396 | -0.000008 | -0.029548 | -0.000007 | -0.025759 |
| 0.00053 | -0.000036 | -0.067969 | -0.000029 | -0.055167 | -0.000026 | -0.048056 |
| 0.00079 | -0.000079 | -0.099817 | -0.000064 | -0.080998 | -0.000055 | -0.070501 |
| 0.00102 | -0.000131 | -0.128486 | -0.000106 | -0.104239 | -0.000092 | -0.090665 |
| 0.00119 | -0.000179 | -0.150320 | -0.000146 | -0.121932 | -0.000127 | -0.105994 |
| 0.00140 | -0.000247 | -0.175916 | -0.000200 | -0.142665 | -0.000174 | -0.123936 |
| 0.00174 | -0.000376 | -0.216610 | -0.000305 | -0.175611 | -0.000265 | -0.152392 |
| 0.00208 | -0.000538 | -0.258169 | -0.000436 | -0.209232 | -0.000378 | -0.181364 |
| 0.00316 | -0.001212 | -0.383673 | -0.000981 | -0.310610 | -0.000847 | -0.268270 |
| 0.00428 | -0.002180 | -0.509179 | -0.001763 | -0.411730 | -0.001516 | -0.354204 |
| 0.00533 | -0.003313 | -0.621394 | -0.002676 | -0.501891 | -0.002293 | -0.430099 |
| 0.00631 | -0.004554 | -0.721577 | -0.003674 | -0.582155 | -0.003136 | -0.497000 |
| 0.00736 | -0.006058 | -0.823655 | -0.004882 | -0.663684 | -0.004150 | -0.564215 |
| 0.00833 | -0.007622 | -0.914701 | -0.006134 | -0.736154 | -0.005193 | -0.623234 |
| 0.00940 | -0.009487 | -1.009178 | -0.007625 | -0.811066 | -0.006424 | -0.683398 |
| 0.01057 | -0.011707 | -1.107104 | -0.009394 | -0.888347 | -0.007872 | -0.744390 |
| 0.01134 | -0.013244 | -1.167710 | -0.010615 | -0.935957 | -0.008861 | -0.781315 |
| 0.01277 | -0.016258 | -1.273333 | -0.013003 | -1.018445 | -0.010774 | -0.843848 |
| 0.01375 | -0.018425 | -1.340439 | -0.014714 | -1.070461 | -0.012125 | -0.882116 |
| 0.01476 | -0.020743 | -1.405425 | -0.016537 | -1.120474 | -0.013546 | -0.917821 |
| 0.01563 | -0.022791 | -1.457781 | -0.018143 | -1.160450 | -0.014781 | -0.945400 |
| 0.01692 | -0.025858 | -1.528371 | -0.020536 | -1.213779 | -0.016588 | -0.980451 |

**Table 9**. Calculated values of $V_e^*$ and $V_e^*/r$ for 2-butanol at all temperatures.

| | 0°C | | 5°C | | 10°C | |
|---|---|---|---|---|---|---|
| $r$ | $V_e^*$ | $V_e^*/r$ | $V_e^*$ | $V_e^*/r$ | $V_e^*$ | $V_e^*/r$ |
| 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| 0.000433 | -0.000032 | -0.073004 | -0.000030 | -0.069942 | -0.000029 | -0.067067 |
| 0.001065 | -0.000190 | -0.178302 | -0.000182 | -0.170671 | -0.000174 | -0.163501 |
| 0.001773 | -0.000523 | -0.294951 | -0.000500 | -0.282042 | -0.000479 | -0.269901 |
| 0.003499 | -0.002005 | -0.572835 | -0.001912 | -0.546381 | -0.001825 | -0.521445 |
| 0.005185 | -0.004330 | -0.835171 | -0.004120 | -0.794570 | -0.003921 | -0.756219 |
| 0.007041 | -0.007842 | -1.113857 | -0.007439 | -1.056618 | -0.007058 | -1.002440 |
| 0.008785 | -0.012000 | -1.366032 | -0.011351 | -1.292146 | -0.010735 | -1.222084 |
| 0.010604 | -0.017169 | -1.619097 | -0.016191 | -1.526798 | -0.015261 | -1.439120 |
| 0.012486 | -0.023349 | -1.870013 | -0.021945 | -1.757548 | -0.020609 | -1.650532 |
| 0.014428 | -0.030552 | -2.117474 | -0.028611 | -1.983001 | -0.026762 | -1.854832 |
| 0.016332 | -0.038357 | -2.348645 | -0.035790 | -2.191423 | -0.033339 | -2.041348 |
| 0.018228 | -0.046804 | -2.567744 | -0.043504 | -2.386703 | -0.040350 | -2.213648 |
| 0.020555 | -0.057994 | -2.821430 | -0.053639 | -2.609571 | -0.049470 | -2.406732 |
| 0.022507 | -0.068003 | -3.021368 | -0.062622 | -2.782301 | -0.057464 | -2.553125 |
| 0.024512 | -0.078788 | -3.214294 | -0.072212 | -2.946021 | -0.065901 | -2.688537 |
| 0.026343 | -0.089029 | -3.379650 | -0.081229 | -3.083568 | -0.073736 | -2.799095 |
| 0.028321 | -0.100446 | -3.546669 | -0.091175 | -3.219318 | -0.082258 | -2.904467 |
| 0.030479 | -0.113226 | -3.714940 | -0.102166 | -3.352061 | -0.091517 | -3.002653 |
| 0.033108 | -0.129138 | -3.900515 | -0.115623 | -3.492309 | -0.102593 | -3.098764 |
| 0.035008 | -0.140780 | -4.021325 | -0.125294 | -3.578965 | -0.110351 | -3.152128 |
| 0.037246 | -0.154543 | -4.149218 | -0.136513 | -3.665152 | -0.119100 | -3.197629 |
| 0.039586 | -0.168886 | -4.266325 | -0.147929 | -3.736934 | -0.127670 | -3.225155 |
| 0.041726 | -0.181869 | -4.358618 | -0.157985 | -3.786210 | -0.134876 | -3.232394 |
| 0.043891 | -0.194768 | -4.437516 | -0.167669 | -3.820100 | -0.141430 | -3.222270 |
| 0.046784 | -0.211475 | -4.520261 | -0.179666 | -3.840354 | -0.148836 | -3.181366 |

| | 15°C | | 20°C | | 25°C | |
|---|---|---|---|---|---|---|
| $r$ | $V_e{}^*$ | $V_e{}^*/r$ | $V_e{}^*$ | $V_e{}^*/r$ | $V_e{}^*$ | $V_e{}^*/r$ |
| 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| 0.000433 | -0.000028 | -0.063791 | -0.000026 | -0.059783 | -0.000022 | -0.051632 |
| 0.001065 | -0.000165 | -0.155355 | -0.000155 | -0.145452 | -0.000134 | -0.125472 |
| 0.001773 | -0.000454 | -0.256151 | -0.000425 | -0.239556 | -0.000366 | -0.206369 |
| 0.003499 | -0.001727 | -0.493414 | -0.001610 | -0.460150 | -0.001382 | -0.395033 |
| 0.005185 | -0.003699 | -0.713402 | -0.003439 | -0.663385 | -0.002942 | -0.567473 |
| 0.007041 | -0.006635 | -0.942373 | -0.006149 | -0.873356 | -0.005238 | -0.743961 |
| 0.008785 | -0.010057 | -1.144881 | -0.009290 | -1.057483 | -0.007880 | -0.897027 |
| 0.010604 | -0.014242 | -1.343083 | -0.013106 | -1.235961 | -0.011066 | -1.043516 |
| 0.012486 | -0.019154 | -1.533992 | -0.017554 | -1.405888 | -0.014744 | -1.180813 |
| 0.014428 | -0.024760 | -1.716036 | -0.022590 | -1.565653 | -0.018863 | -1.307382 |
| 0.016332 | -0.030698 | -1.879663 | -0.027876 | -1.706833 | -0.023134 | -1.416502 |
| 0.018228 | -0.036968 | -2.028103 | -0.033399 | -1.832310 | -0.027533 | -1.510512 |
| 0.020555 | -0.045024 | -2.190456 | -0.040403 | -1.965653 | -0.033008 | -1.605871 |
| 0.022507 | -0.051988 | -2.309828 | -0.046365 | -2.059979 | -0.037562 | -1.668862 |
| 0.024512 | -0.059229 | -2.416339 | -0.052458 | -2.140118 | -0.042095 | -1.717352 |
| 0.026343 | -0.065842 | -2.499461 | -0.057916 | -2.198560 | -0.046030 | -1.747337 |
| 0.028321 | -0.072901 | -2.574072 | -0.063606 | -2.245867 | -0.049970 | -1.764380 |
| 0.030479 | -0.080385 | -2.637407 | -0.069451 | -2.278683 | -0.053788 | -1.764777 |
| 0.033108 | -0.089033 | -2.689189 | -0.075890 | -2.292216 | -0.057595 | -1.739614 |
| 0.035008 | -0.094846 | -2.709241 | -0.079956 | -2.283895 | -0.059650 | -1.703878 |
| 0.037246 | -0.101092 | -2.714155 | -0.083976 | -2.254625 | -0.061193 | -1.642928 |
| 0.039586 | -0.106789 | -2.697674 | -0.087148 | -2.201509 | -0.061650 | -1.557387 |
| 0.041726 | -0.111127 | -2.663234 | -0.088992 | -2.132744 | -0.060903 | -1.459573 |
| 0.043891 | -0.114538 | -2.609584 | -0.089696 | -2.043596 | -0.058887 | -1.341650 |
| 0.046784 | -0.117351 | -2.508372 | -0.088596 | -1.893728 | -0.054002 | -1.154283 |