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A Volumetric Study of Aqueous Butanol Solutions

Priyanka P. Chary
Scripps College

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Priyanka Chary

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Thesis Readers:

Dr. Anthony Fucaloro

Dr. Mary Hatcher-Skeers

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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 ρ, as reported by Fucaloro et al., is:

$$V = \frac{n_1 M_1 + n_2 M_2}{\rho} \tag{1}$$

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

$$V_{tot} = n_1 V_1 + n_2 V_2 \tag{2}$$

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

$$V^* = \frac{V_{tot}}{n_1} = \frac{V}{x_1} = \frac{M_1 + rM_2}{\rho} = V_1 + rV_2, \tag{3}$$

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

$$V_{ideal}^{*} = V_1^{\cdot} + rV_2^{\circ} \,, \tag{4}$$

where $V_1^{\cdot}$ is the molar volume of pure water, and $V_2°$ 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

$$V_e^{*} = V^{*} - V_{ideal}^{*} \tag{5}$$

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 $q = q_A + q_B$:

$$S + qW \rightarrow SW_q \tag{6}$$

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}):

$$V_{tot} = V_1^{\cdot}[n_1 - n_2(q_A + q_B)] + n_2 V_{SW(qA+qB)} \tag{7}$$

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

$$V^* = \frac{V_{tot}}{n_1} = V_1^{\cdot} + r\left[V_{SW(qA+qB)} - V_1^{\cdot}(q_A + q_B)\right] \tag{8}$$

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

$$V_{SW(qA+qB)} = V_2^{int} + V_2^{void} + q_A V_{1A}^{solv} + q_B V_{1B}^{solv} \tag{9}$$

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 $V_1^{\cdot} + rV_2^{\circ}$. 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,

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

(12)

Combining Equations 5, 11 and 12 gives

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

(13)

or

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

(14)

Several assumptions are made in this analysis, namely:

- ΔV_{1A} and ΔV_{1B} are functions of temperature,
- ΔV_{1A} and ΔV_{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
- $\frac{dq_A}{dr}$ and $\frac{dq_B}{dr} < 0$.

V. Relating Data to Model

Equation 2 reveals how V* may be calculated from the mole ratio r and density, ρ. 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,

$$V^* = a + br + cr^2 + er^3 + fr^4 \tag{15}$$

where a = the molar volume of pure water, $V_1^{\cdot}$, and b = $V_2°$, 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

$$V^*_{ideal} = a + br = V_1^{\cdot} + rV_2^{\circ} \tag{16}$$

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

$$V_e^* = V^* - V^*_{ideal} = cr^2 + er^3 + fr^4 \tag{17}$$

Dividing by the mole ratio gives an expression

$$\frac{V_e^*}{r} = cr + er^2 + fr^3 \tag{18}$$

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.

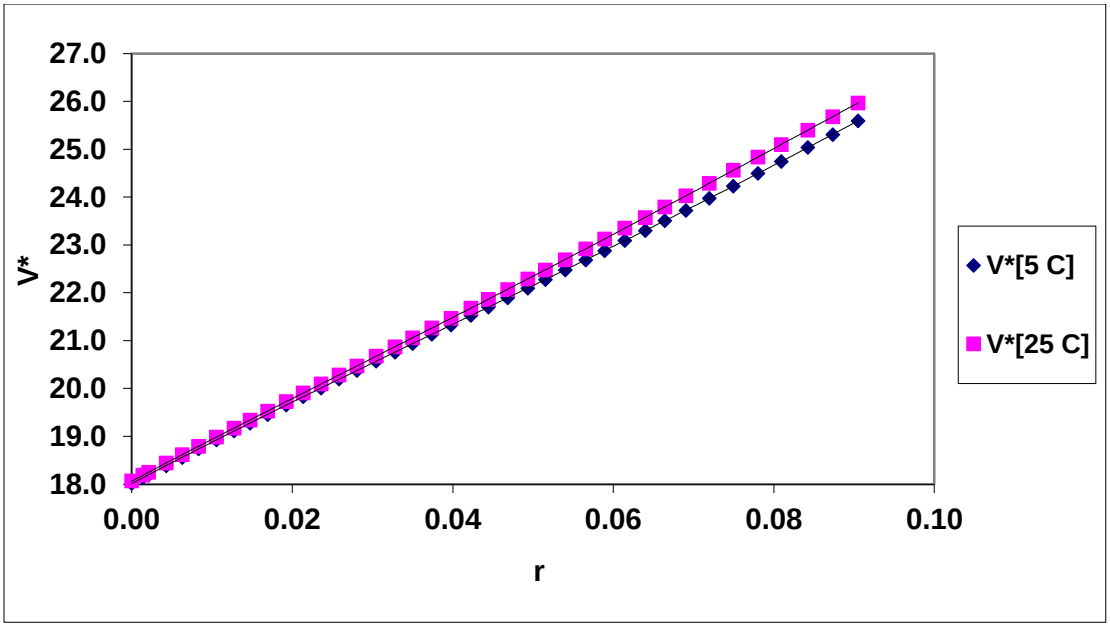

Figure 1. The graph of V* vs. r for tert-butanol at 5°C and 25°C.

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*	*ρ*	*V**	*ρ*	*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*	
ρ	V^*	ρ	V^*	ρ	V^*	ρ	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 (^{o}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 (^{o}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 (^{o}C)	a ($V_1^{\bullet}$)	b (V_2°)	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 $V_1^{\cdot}$, 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 $V_2°$, the partial molar volume of alcohol at infinite dilution (the limit as r approaches zero). The structure of the alcohol caused little variation in $V_2°$. 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.

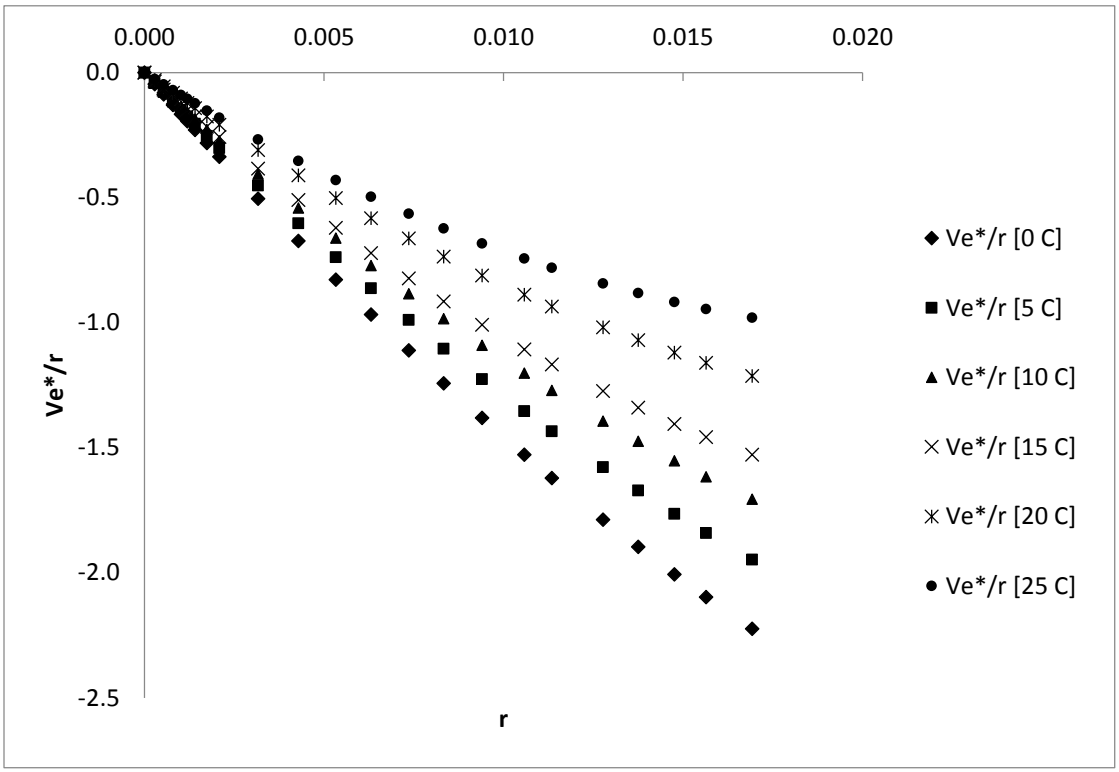

Figure 2. The graph of V_e*/r vs. r for 1-butanol at all six temperatures.

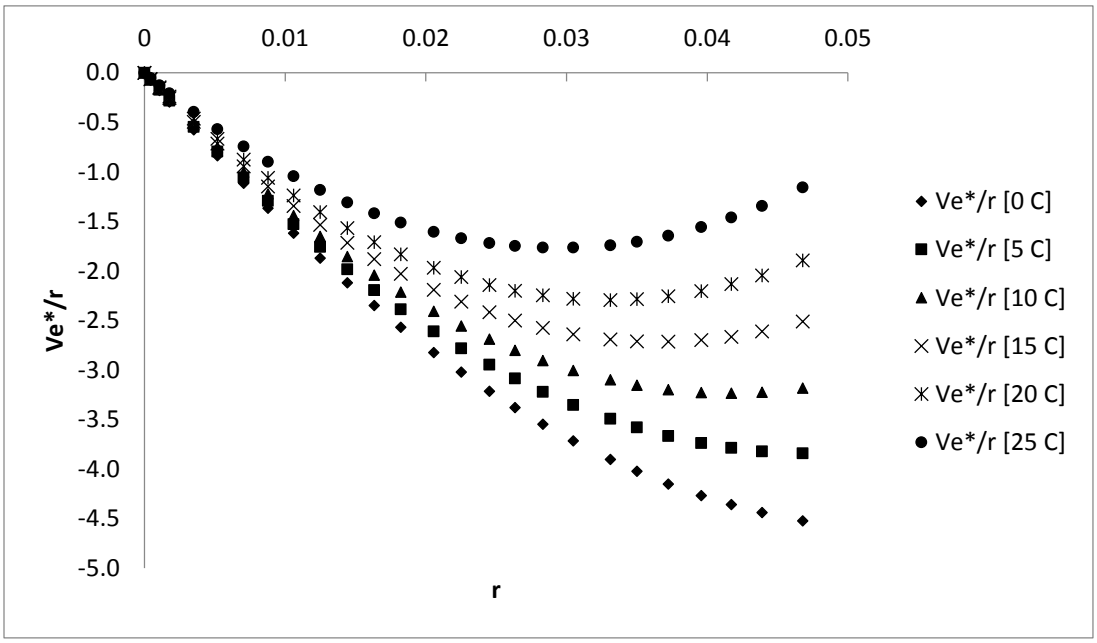

Figure 3. The graph of V_e*/r vs. r for 2-butanol at all six temperatures.

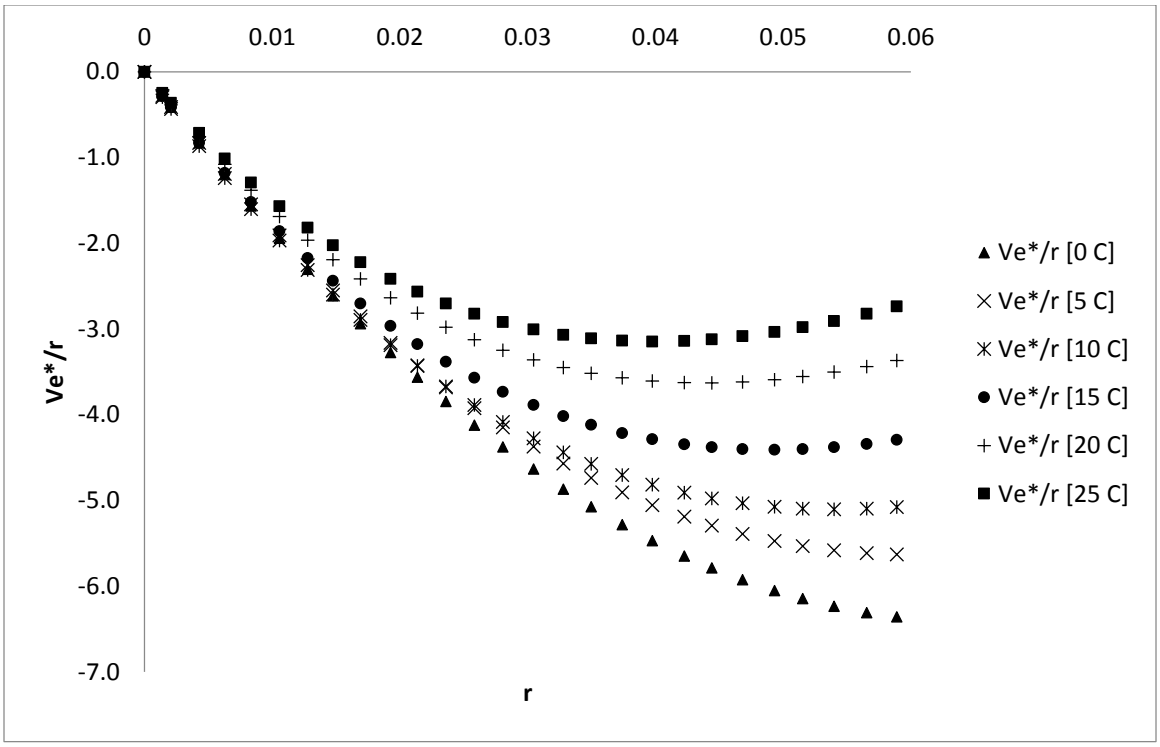

Figure 4. The graph of V_e*/r vs. r for tert-butanol at all six temperatures. As temperature decreases, the concentration curve becomes steeper.

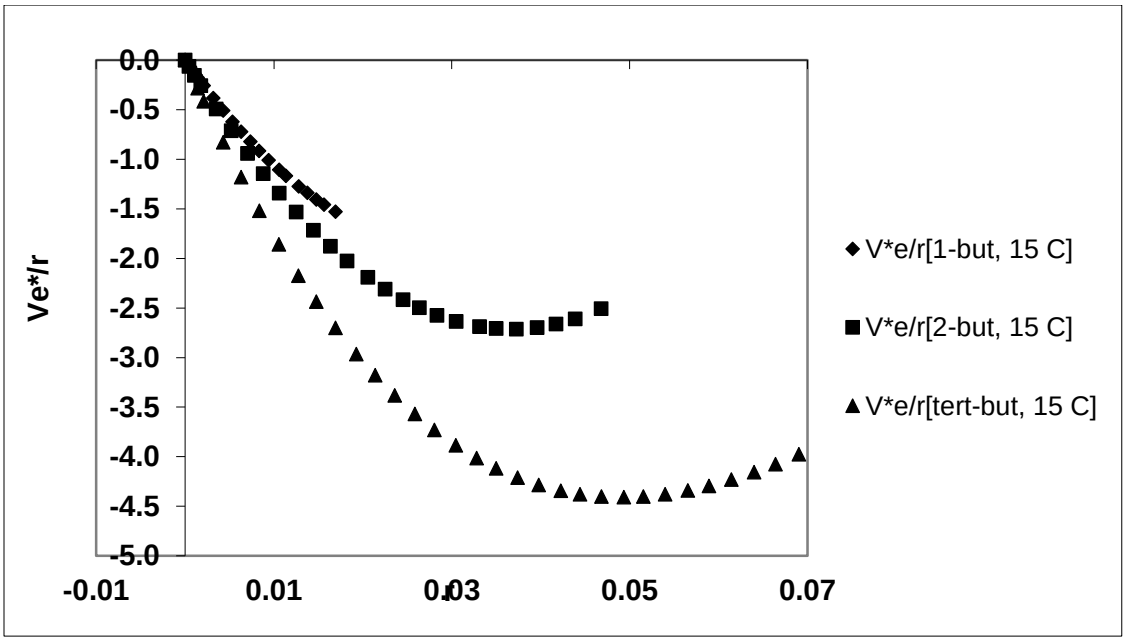

Figure 6. The graph of V_e*/r vs. r for all three butanols at 15°C. The concentration curve becomes steeper as the alcohol group is shifted from a primary carbon to a secondary position to a tertiary position. The rest of our data is consistent with this graph.

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, $q_A°$ and $q_B°$ will always be the maximum values of q_A and q_B, making the q terms in equation 14 negative. ΔV_{1A} is a positive term, since the hydrocarbon chain acts as a solvent structure maker, and ΔV_{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 ΔV_{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 ΔV_{1B}, ΔV_{1A} and $(q_B-q_B°)$ are independent of isomer, then we conclude that $|(q_A-q_A°)|$ 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*	*ρ*	*V**	*ρ*	*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*	
ρ	*V**	*ρ*	*V**	*P*	*V**	*ρ*	*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*	*ρ*	*V**	*ρ*	*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*	
ρ	*V**	ρ	*V**	ρ	*V**	ρ	*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