Partial Molal Volume and Viscosity Study Of Vitamin B₁ and B₃ In Water At Different Temperatures

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Abstract
Solute-solvent interaction was investigated in this study using the vitamins B₁ and B₃ as solutes in water as a solvent at four different temperatures.

The study covered theoretical calculations concerning partial molal volume, Van der Waals volume and some related parameters as well as experimental measurements; a comparison and discussion was made, viscosity measurements have been performed for the above system.

The applicability of Jones-dole equation has been discussed in terms of concentration and temperature effects and then related to the results of partial molal volume.

Introduction
The effect of elevated amounts of vitamins as solutes in the body is of significant importance; certain diseases could develop as a result of decreasing the concentration of some vitamins.

This fact leads us to study first the nature of interaction between the vitamins (the solute) and aqueous body fluids (the solvent). The limiting partial molal volume ({$\tilde{V}_o$} ) and viscosity ({$\eta$} ) have been utilized to account for the nature of solute-solvent interaction using aqueous and mixed solvents.(2-9)

Edwards and Farrell (10) and Tera Sawa et. al (11) had shown that ($V^o$) may be estimated as well as the detection of solute-solvent interaction provided that the intrinsic volume of solute molecule is made equal to its Van der Waals volume ($v_w$). Assuming the solute molecule of a spherical shape possessing an apparent volume of ($V^o$) where ($v^o = V^o / N$ ); (N) is Avogador’s number.

The volume of ($v^o$) is greater than ($v_w$) by an amount of associated empty volume or void volume as given by equation (1).

{$\tilde{v}_o = 4 \pi (r_w + \Delta )^3 / 3$} ..........(1)

Where ($r_w$) is the radius of Van der Waals volume, which is equal to $r_w=(3v_w / 4 \pi)^{1/3}$

The term ({$\Delta$}) represents the thickness of spherical shell which forms the void volume. Hydrophilic compounds exhibit lower values for ({$\Delta$}) as a consequence of hydrogen bonding between solvent molecules (water) and the polar groups of solute molecules (12) leading to a shrinkage in ({$\Delta$}) and hence in ($v^o$). Terra Sawa et. al (13) have reported equation (2):

{$\tilde{V}_o = a V_w + b$} .................(2)

Where ($V_w$) is the molar Van der Waals volume, which represents an intrinsic volume occupied by one mole

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of solute molecules and (a) and (b) are empirical constants.

Equations (1) and (2) have been utilized to account for a theoretical predication to the system under investigation.

The results were compared with the experimental results of the apparent molal volume \( V^a \) calculated from equation (3) and fitted to equation (4) by the least squares method:

\[
\bar{V} = \frac{1}{M} \left[ \frac{1000 + m M}{d} - \frac{1000}{d_0} \right] \quad \text{(3)}
\]

\[
\bar{V} = V^a + a m \quad \text{(4)}
\]

Where \( M \) = molecular weight of the solute.

\( m \) = molality of the solution,

\( d \) = density of the solution,

\( d_0 \) = density of the solvent,

and \( a \) = constant.

Viscometric study of this system involved making use of Jones-Dole equation of the form:

\[
\eta = \eta_0 + BC + DC^2 \quad \text{(5)}
\]

Where \( C \) is the molarity of solution of dipolar ions or non-electrolytes; \( \eta \) and \( \eta_0 \) are the absolute viscosities of solution and solvent respectively and (B) and (D) are empirical coefficients.

The coefficient (B) represents the effects of size and shape of solute molecules as well as the structural effect induced as a consequence of solute-solvent interaction.\(^{(14)}\)

The significance of (D) coefficients is still not clear. Effective flow volumes \( V_h \) may be calculated from the equation:

\[
V_h = \frac{B}{a} \quad \text{(6)}
\]

Where (a) is the shape factor which is taken to be 2.5 for spherical particles.

Alternatively, the effective flow volume can be calculated from the equation reported by Vand \(^{(15)}\) and modified by Eagland and Pilling \(^{(16)}\):

\[
\frac{C}{\log \left( \frac{\eta}{\eta_0} \right)} = \frac{2.303}{a V_h} \quad \text{(7)}
\]

where \( Q \) is the interaction coefficient.

Experimental:

(a) **Materials**

Vitamins B\(_1\) (Thiamin) and B\(_3\) (niacin) obtained from the general company for drug industries and medical appliance in samara-Iraq. Vitamin aqueous solutions in the concentration range of study have been prepared in the normal way.

(b) **Measurements**

Densities were determined using Anton paar(DMA 602) digital densimeter, thermostated to \( \pm 0.01 \) °C. The overall precision of measurements was estimated to be better than \( \pm 2 \times 10^{-6} \) gm/ml.

Viscosities were determined using a suspended level ubbelohde viscometer. The flow times were recorded electronically with an electronic timer of precision \( \pm 0.01 \)s and the temperature of the bath was
controlled better than ±0.01 °C. The instrument was calibrated with distilled water. Flow times were reproducible to 0.01 S.

Result and Discussion

Density values of aqueous solutions of vitamins (B₁) and (B₃) are given in table (1) as function of molal concentration at four different temperature. Making use of equation (3), apparent molal volume values of vitamins B₁ and B₃ have been calculated and presented in table (2). Fitting the data of table 2 to equation (4) by the method of least squares produced the limiting partial molal volume at each temperature of study as shown in table (3). The data of table (2) is presented in graphical forms and shown in figures (1a) and (1b) for vitamins B₁ and B₃. Theoretical calculations have been done to estimate Vander Waals volumes \( v_w \) and partial molal volumes \( v_p \) of the two vitamins. Following the principle of additivity reported by Bondi \(^{17,18}\) and Edward \(^{19}\), \( v_w \) was calculated and considered dissected into contributions from individual atoms or groups of atoms measured in (ml/mole). Vander Waals volume of vitamins B₃ molecule for example, is calculated from contributions of

\[
\begin{align*}
\text{O} & \quad \| \\
\text{N} & \quad - \quad \text{C} \quad - \\
\text{C} & \quad \| \\
\text{H} & \quad \text{by} \quad 5.2, 11.7, 10.54, 4.74 \\
\text{and} & \quad 8.06 \text{ ml/mole}
\end{align*}
\]

Respectively and is equal to 64.42 ml/mol. Similarly \( v_w \) value of vitamin B₁ (molecules) is 146.33 ml/mol. The corresponding \( v_w \) and \( r_w \) values of vitamins B₁ and B₃ molecules are:

146.33 ml/mole & \( 3.872 \times 10^8 \) cm for vitamin B₁ molecules 64.42ml/mol & \( 2.945 \times 10^8 \) cm for vitamin B₃ molecules.

In order to calculate the limiting partial molal volume of the two vitamins, strong interaction is expected between the solute molecules and the solvent molecular arrangements due to the polarity and possibility of hydrogen bonds formation. As a consequence of this, an appreciable shirin kag in \( \Delta \) and hence in \( (V^\theta) \) is expected to take place. If we assume \( \Delta \) to posses a value of the order of magnitude in the range \( (0.6-0.7) \times 10^{-8} \) cm the two vitamins molecules, equation (1) would predict:

\[
\begin{align*}
\Delta & = 4.09 \times 10^{-2} \text{ ml/molecule} \\
\Delta & = 226.49 \text{ ml/mol} \\
\Delta & = 19 \times 10^{-2} \text{ ml/molecule} \\
\Delta & = 115.7472 \text{ ml/mole}
\end{align*}
\]

for vitamin B₁ molecules

These calculated theoretical values of \( (V^\theta) \) are of similar magnitudes of the corresponding experimental values given in table 4 indicating the assumed values mentioned above for \( \Delta \) are acceptable. Alternatively, precise estimation of \( \Delta \) may be done from equation (8) which could be derived from equation (1)

\[
(\sqrt{v^\theta} / v_w)^{1/2} = 1 + \frac{1}{r_w} \quad \cdots \cdots (8)
\]

substituting the experimental values of \( (V^\theta) \) and the calculated values of \( (v_w) \) and \( (r_w) \) in equation (8), \( \Delta \) values were estimated and found quite close to assumed values for B₁ and B₃.

The variation of viscosity \( (\eta) \) in (cp) as a function of molar concentration of vitamins B₁ and B₃ at
the our temperatures of study are
given in table(5).

Making use of equation (5) and
ignoring the term DC², linear
relationships were obtained by plotting
(ηr - 1) \(\sqrt{c}\) values versus the square
root of \(c\) molar concentration as
shown in figure (2).

The estimated (B) coefficient values
are shown in table (6). These values
may be viewed through high solutesolvent interaction exhibiting the effect
of structure breaking of solvent
molecules arrangements by the
molecules of the solute.

Effective flow volumes \(\left(V_b\right)\)
were calculated from equation (7)
assuming these vitamins as spherical
particles. Thus, plotting c/ log (ηr / ηc )
vs. (c) produce straight lines of slope (2.303 Q/a) and intercept (2.303 / Vc) as
shown in figure (3). Table (7) indicate the effective flow volumes at
four different temperature (293 –308) K .

The results of this study suggest that, the contribution of two vitamins in the B value was found
negative which may viewed as a
structure breaker to the arrangements
of solvent molecules.

<table>
<thead>
<tr>
<th>C/mol L-1</th>
<th>293.15 K</th>
<th>298.15 K</th>
<th>303.15 K</th>
<th>308.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent H2O</td>
<td>0.999823</td>
<td>0.99707</td>
<td>0.99568</td>
<td>0.99406</td>
</tr>
<tr>
<td>0.01</td>
<td>1.00128</td>
<td>0.99991</td>
<td>0.99716</td>
<td>0.99561</td>
</tr>
<tr>
<td>0.02</td>
<td>1.00255</td>
<td>0.99929</td>
<td>0.99753</td>
<td>0.99592</td>
</tr>
<tr>
<td>0.03</td>
<td>1.00331</td>
<td>0.99977</td>
<td>0.99893</td>
<td>0.99639</td>
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<tr>
<td>0.04</td>
<td>1.00432</td>
<td>1.00106</td>
<td>1.00042</td>
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</tr>
<tr>
<td>0.05</td>
<td>1.00541</td>
<td>1.00203</td>
<td>1.00159</td>
<td>0.99913</td>
</tr>
</tbody>
</table>

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<th>303.15 K</th>
<th>308.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent H2O</td>
<td>0.999823</td>
<td>0.99707</td>
<td>0.99548</td>
<td>0.99406</td>
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<tr>
<td>0.01</td>
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<td>0.99753</td>
<td>0.99605</td>
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<td>0.04</td>
<td>1.00257</td>
<td>0.99952</td>
<td>0.99815</td>
<td>0.99595</td>
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<tr>
<td>0.05</td>
<td>1.00309</td>
<td>0.99948</td>
<td>0.99830</td>
<td>0.99760</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C/mol L-1</th>
<th>298.15 K</th>
<th>303.15 K</th>
<th>308.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>Vo</td>
<td>m</td>
<td>Vo</td>
</tr>
<tr>
<td>0.02</td>
<td>245.42712</td>
<td>202.75241</td>
<td>0.02018</td>
</tr>
<tr>
<td>0.03</td>
<td>242.11381</td>
<td>229.36338</td>
<td>0.03037</td>
</tr>
<tr>
<td>0.04</td>
<td>239.00668</td>
<td>218.74988</td>
<td>0.04053</td>
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<tr>
<td>0.05</td>
<td>239.59684</td>
<td>218.85330</td>
<td>0.05026</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C/mol L-1</th>
<th>298.15 K</th>
<th>303.15 K</th>
<th>308.15 K</th>
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</thead>
<tbody>
<tr>
<td>m</td>
<td>Vo</td>
<td>m</td>
<td>Vo</td>
</tr>
<tr>
<td>0.02</td>
<td>95.36990</td>
<td>68.38394</td>
<td>0.02016</td>
</tr>
<tr>
<td>0.03</td>
<td>87.69311</td>
<td>67.38895</td>
<td>0.03026</td>
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<tr>
<td>0.04</td>
<td>76.67290</td>
<td>60.61003</td>
<td>0.04026</td>
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<tr>
<td>0.05</td>
<td>75.12384</td>
<td>59.96158</td>
<td>0.05047</td>
</tr>
</tbody>
</table>
Table 3: Limiting molal volume values of B1 and B3 in water at different temperatures (298-308) K.

<table>
<thead>
<tr>
<th>Vitamins</th>
<th>298.15 K</th>
<th>303.15 K</th>
<th>308.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>246.556</td>
<td>237.722</td>
<td>247.819</td>
</tr>
<tr>
<td>B3</td>
<td>115.856</td>
<td>91.3287</td>
<td>119.845</td>
</tr>
</tbody>
</table>

Table 4: Theoretical and calculate values for limiting partial molal volume ($\Phi_v$).

<table>
<thead>
<tr>
<th>Vitamins</th>
<th>$\Phi_v$ Calculations</th>
<th>$\Phi_v$ Exper.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitamin B1</td>
<td>246.556</td>
<td>246.556</td>
</tr>
<tr>
<td>Vitamin B3</td>
<td>115.762</td>
<td>115.856</td>
</tr>
</tbody>
</table>

Table 5a: Viscosities of B1 solutions in water as a function of molar concentration at different temperatures (293-308) K.

<table>
<thead>
<tr>
<th>C/mol.L⁻¹</th>
<th>293.15 K</th>
<th>298.15 K</th>
<th>303.15 K</th>
<th>308.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent H2O</td>
<td>1.002</td>
<td>0.8904</td>
<td>0.7975</td>
<td>0.7194</td>
</tr>
<tr>
<td>0.01</td>
<td>2.03939</td>
<td>1.91923</td>
<td>1.84014</td>
<td>1.77190</td>
</tr>
<tr>
<td>0.02</td>
<td>2.11937</td>
<td>2.101930</td>
<td>1.84611</td>
<td>0.02453</td>
</tr>
<tr>
<td>0.03</td>
<td>2.26904</td>
<td>2.10753</td>
<td>2.04297</td>
<td>2.00531</td>
</tr>
<tr>
<td>0.04</td>
<td>2.31043</td>
<td>2.20734</td>
<td>2.15536</td>
<td>2.03528</td>
</tr>
<tr>
<td>0.05</td>
<td>2.41404</td>
<td>2.33405</td>
<td>2.23130</td>
<td>2.13850</td>
</tr>
</tbody>
</table>

Table 5b: Viscosities of B3 solutions in water as a function of molar concentration at different temperatures (293-308) K.

<table>
<thead>
<tr>
<th>C/mol.L⁻¹</th>
<th>293.15 K</th>
<th>298.15 K</th>
<th>303.15 K</th>
<th>308.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent H2O</td>
<td>1.002</td>
<td>0.8904</td>
<td>0.7975</td>
<td>0.7194</td>
</tr>
<tr>
<td>0.01</td>
<td>1.59634</td>
<td>1.51930</td>
<td>1.48012</td>
<td>1.40037</td>
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<td>0.02</td>
<td>1.67450</td>
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<tr>
<td>0.03</td>
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<td>1.65062</td>
<td>1.61945</td>
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<td>0.04</td>
<td>1.82310</td>
<td>1.71509</td>
<td>1.67931</td>
<td>1.60987</td>
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<tr>
<td>0.05</td>
<td>1.91089</td>
<td>1.76904</td>
<td>1.73537</td>
<td>1.66882</td>
</tr>
</tbody>
</table>

Table 6: B-coefficient values for B1 and B3 at different temperature (293-308) K.

<table>
<thead>
<tr>
<th>Vitamins</th>
<th>293.15 K</th>
<th>298.15 K</th>
<th>303.15 K</th>
<th>308.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitamin B1</td>
<td>-31.95000</td>
<td>-34.17200</td>
<td>-40.12640</td>
<td>-51.24270</td>
</tr>
<tr>
<td>Vitamin B3</td>
<td>-14.97800</td>
<td>-16.81750</td>
<td>-26.44540</td>
<td>-37.79870</td>
</tr>
</tbody>
</table>

Table 7: Effective flow volume value calculated from equation $C\log(\eta / \eta_0) = 2.303 / Vh - 2.303 QC/a$ for B1 and B3 at different temperature (293-308) K.

<table>
<thead>
<tr>
<th>Vitamins</th>
<th>293.15 K</th>
<th>298.15 K</th>
<th>303.15 K</th>
<th>308.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>0.01163</td>
<td>0.01772</td>
<td>0.009347</td>
<td>0.00795</td>
</tr>
<tr>
<td>B3</td>
<td>0.02413</td>
<td>0.01724</td>
<td>0.01296</td>
<td>0.01349</td>
</tr>
</tbody>
</table>
Fig. 1 a - apparent molal volume ($\phi^* v$) for $B_1$ a(298), b(303), c(308) k

Fig. 1 b - apparent molal volume ($\phi^* v$) for $B_2$ a(298), b(303), c(308) k

(a) Vitamin B1

(b) Vitamin B3

Fig. 2: $(n - 1) / \sqrt{c}$ values versus $\sqrt{c}$ for $B_1$ and $B_2$ at different temperature (293 – 308) K.
Fig 3. a: \( c/\log \eta_r \) values versus (c) for \( B_i \) for concentration range (0.01 - 0.05) \( \text{mol L}^{-1} \) at different temperatures (293-308) K.

Fig 3. b: \( c/\log \eta_r \) values versus (c) for \( B_i \) for concentration range (0.01 - 0.05) \( \text{mol L}^{-1} \) at different temperatures (293-308) K.
References


دراسة الحجم المولاري الجزئي واللزوجة لفيتامينات B1 و B3 في الماء عند درجات حرارية مختلفة

سعود عبد العزيز عيسى و إلخانم حمد فرحان و هلال حمدي

دكتوراه، قسم الكيمياء الحياتية، كلية الطب، جامعة النهرين
دكتوراه، قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد
كلية الصيدلة، الجامعة المستنصرية

الخلاصة

تم بحث تداخل المذيب المذيب في هذه الدراسة باستخدام (B1, B3) كمذيب والماء كمذيب عند أربع درجات حرارية، شملت الدراسة الحسابات النظرية للحجم المولاري الجزئي، وحجم فالدرفال وعلاقتها مع بعضها ومقدارها مع القياسات العملية وملاحظتها. وتم قياس اللزوجة للمحتوى المختارة وتطبيق معادلة جونز - مول ومحاسبتها مع التركيز ودرجات الحرارة وعلاقتها مع الحجم المولاري الجزئي.