Partial Molal Volume and Viscosity Study Of Vitamin B_1 and B_3 In Water At Different Temperatures

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Abstract

Solute-solvent interaction was investigated in this study using the vitamins B_1 and B_3 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 ($\overline{V^o}$) and viscosity (η) 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).

$$\overline{vo} = 4 \pi (r_w + \Delta)^3 / 3 \quad \text{.....(1)}$$

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

$$\overline{V^o} = a V_w + b \quad \text{.....(2)}$$

Where (V_w) is the molar Van dar 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^o) calculated from equation (3) and fitted to equation (4) by the least squares method:-

$$\overline{V} = \frac{1}{M}\left[\frac{1000 + m\,M}{d} - \frac{1000}{d_o}\right] \quad ..(3)$$

$$\overline{V} = V^o + am \quad .....(4)$$

Where M= molecular weight of the solute.
m= molality of the solution,
d= density of the solution,
d o = density of the solvent,
and a = constant.

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

$$\frac{\eta}{\eta_o} = 1 + BC + DC^2 \quad .....(5)$$

Where C is the molarity of solution of dipolar ions or non-electrolytes; (η) and (η_o) 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.

$$\overline{V}_h = B/a \quad .....(6)$$

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].

$$C/\log\left[\frac{\eta}{\eta_o}\right] = \frac{2.303}{a V_h} - \frac{2.303\,QC}{a} \quad ... (7)$$

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

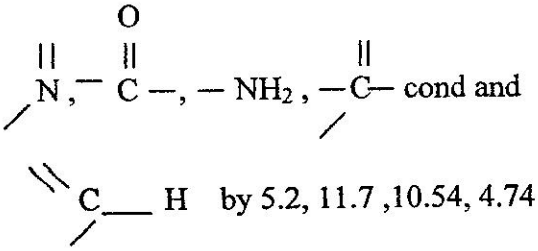
Densities were determined using Anton paar(DMA 602) digital densimeter , thermostated to ± 0.01 °C . The overall precision of measurements was estimated to be better than $\pm 2 \times 10^{-6}$ gm/ml.

Viscosities were determined using a suspended level ubbelohde viscometer.
The flow times were recorded electronically with an electronic timer of precision ±0.01s 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 (B_1) and (B_3) 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 B_1 and B_3 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 ingraphical forms and shown in figures (1a) and (1b) for vitamins B_1 and B_3 . Theoretical calculations have been done to estimate Vander Waals volumes (v_w) and partial molal volumes (V_o) of the two vitamins. Following the principle of addivity 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 B_3 molecule for example, is calculated from contributions of



and 8.06 ml/mole

Respectively and is equal to 64.42 ml/mol. Similarly (v_w) value of vitamin B_1 (molecules) is 146.33 ml/mol. The corresponding (v_w) and (r_w) values of vitamins B_1 and B_3 molecules are:

146.33 ml/mole & 3.872×10^{-8} cm for vitamin B_1 molecules 64.42ml/mol& 2.945×10^{-8} cm for vitamin B_3 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 shrin kag in (Δ) and hence in (V^o) is expected to take place. If we assume (Δ) to posses a value of the order of magnitude in the range (0.6-0.7) x 10^{-8} cm the two vitamins molecules , equation(1) would predict:-

$v^o = 4.09 \times 10^{-22}$ ml/molecule
$v^o = 246.49$ ml/mol
} for vitamin B_1 molecules

$v^o = 1.9 \times 10^{-22}$ ml/molecule
$v^o = 115.7472$ ml/mole
} for vitamins B_3 molecules

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

$$(\bar{v}^o / v_w)^{1/3} = 1 + \frac{\Delta}{r_w} \quad \ldots\ldots(8)$$

substituting the experimental values of ($\bar{v}^o$) and the calculated values of (v_w) and (r_w) in equation (8) , (Δ) values were estimated and found quite close to assumed values for B_1 and B_3

The variation of viscosity (η) in (cp) as a function of molar concentration of vitamins B_1 and B_3 at

the our temperatures of study are given in table(5) .

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

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

Effective flow volumes (V_h) were calculated from equation (7) assuming these vitamins as spherical particles. Thus, plotting c/ log (η / η_o) vs. (c) produce straight lines of slope (2.303 Q/a) and intercept (2.303 / V_h) 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 nagative which may viewed as a structure breaker to the arrangements of solvent molecules.

Table .1. a :- Density values of vitamin B1 as a function of molar concentration at different temperatures. (293 – 308)K.

C/mol.L-1	ρ / (g.cm-3)			
	293.15 K	298.15 K	303.15 K	308.15 K
Solvent H2O	099823	0.99707	0.99568	0.99406
0.01	1.00128	0.99801	0.99716	0.99501
0.02	1.00235	0.99894	0.99839	0.99592
0.03	1.00331	0.99997	0.99895	0.99689
0.04	1.00432	1.00106	1.00042	0.99793
0.05	1.00541	1.00203	1.00159	0.99913

Table .1. b :- Density values of vitamin B3 as a function of molar concentration at different temperatures. (293 – 308)K.

C/mol.L-1	ρ / (g.cm-3)			
	293.15 K	298.15 K	303.15 K	308.15 K
Solvent H2O	0.99823	0.99707	0.99568	0.99406
0.01	1.00047	0.99719	0.99603	0.99396
0.02	1.00116	0.99761	0.99676	0.99443
0.03	1.00189	0.99811	0.99733	0.99520
0.04	1.00257	0.99892	0.99815	0.99595
0.05	1.00309	0.99943	0.99880	0.99760

Table. 2 .a:- Apperant molal volume values of B1 in water at different temperature(298-308)K .

C/mol.L-1	298.15 K		303.15 K		308.15 K	
	m	Vo	m	Vo	m	Vo
0.02	0.01017	245.42712	0.02018	202.75241	0.02018	245.81086
0.03	0.03030	242.11581	0.03030	229.36738	0.03037	244.41175
0.04	0.04050	239.0068	0.04050	219.74988	0.04053	240.49403
0.05	0.05075	239.59684	0.05075	218.85330	0.05026	237.30418

Table. 2 .b:- Apperant molal volume values of B3 in water at different temperature(298-308)K .

C/mol.L-1	298.15 K		303.15 K		308.15 K	
	m	Vo	m	Vo	m	Vo
0.02	0.02009	95.36990	0.02011	68.38394	0.02016	104.2176
0.03	0.03017	87.69311	0.03019	67.38895	0.03026	84.6075
0.04	0.04024	76.07290	0.04027	60.61003	0.04036	75.31032
0.05	0.05034	75.12384	0.05037	59.96158	0.05047	68.50516

Table. 3 :- Limiting molal volume values of B1 and B3 in water at different temperatures (298-308)K .

Vitamins	$\overline{V}o$ (ml/mol) (limiting molal volume)		
	298.15 K	303.15 K	308.15 K
B1	246.556	237. 722	247.819
B3	115.856	91.3287	119.845

Table. 4 :- Theoretical and calculate values for limiting partial molal volume(Φo v) .

Vitamins	Φo v calculations	Φo v Exper.
Vitamin B1	**246.550**	**246.556**
Vitamin B3	**115.762**	**115.856**

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

C/mol.L-1	η / (Cp)			
	293.15 K	298.15 K	303.15 K	308.15 K
Solvent H2O	1.002	0.8904	0.7975	0.7194
0.01	2.03939	1.91923	1.84034	1.77190
0.02	2.11937	1.91930	1.84611	0.02453
0.03	2.26904	2.10753	2.04297	2.00051
0.04	2.31043	2.20734	2.15536	2.05328
0.05	2.41404	2.33405	2.23130	2.13850

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

.C/mol.L-1	η / (Cp)			
	293.15 K	298.15 K	303.15 K	308.15 K
Solvent H2O	1.002	0.8904	0.7975	0.7194
0.01	1.59634	1.51930	1.48012	1.40037
0.02	1.67450	1.57986	1.56192	1.45305
0.03	1.75904	1.65062	1.61945	1.53292
0.04	1.82310	1.71509	1.67931	1.60987
0.05	1.91089	1.76904	1.73537	1.66682

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

.Vitamins	293.15 K	298.15 K	303.15 K	308.15 K
Vitamin B1	**-31.95000**	**-34.17200**	**-40.12640**	**-51.24270**
Vitamin B3	**-14.97880**	**-20.81750**	**-26.44540**	**-27.79870**

Table 7: Effective flow volume value calculated from equation C/ log (η / ηo) = 2.303/a vh – 2.303 QC/a for B1 and B3 at different temperature (293-308) K.

Vitamins	Vh values L.mol-1			
	C/(logη / ηo)= 2.303/a Vh – 2.303QC/a			
	293.15 K	298.15 K	303.15 K	308.15 K
B1	0.01103	0.01772	0.009437	0.00795
B3	0.02413	0.01724	0.01296	0.01349

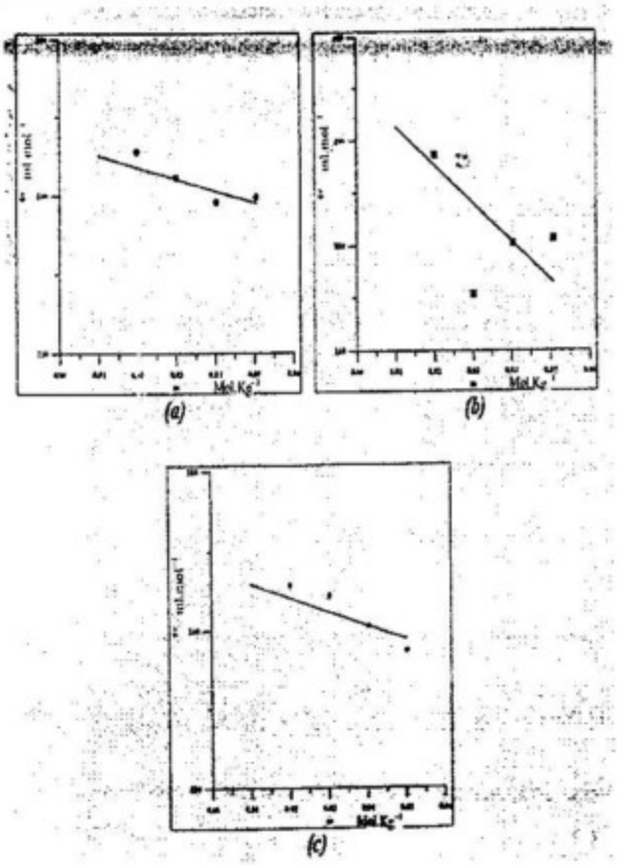


Fig. 1 a :- apparent molal volume ($\Phi^o v$) for B_1 a(298) ,b(303) ,c(308) k

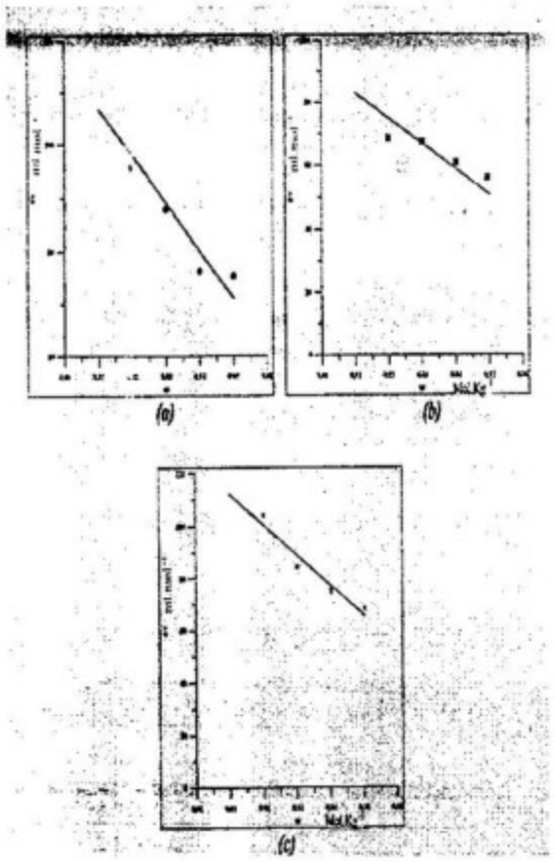
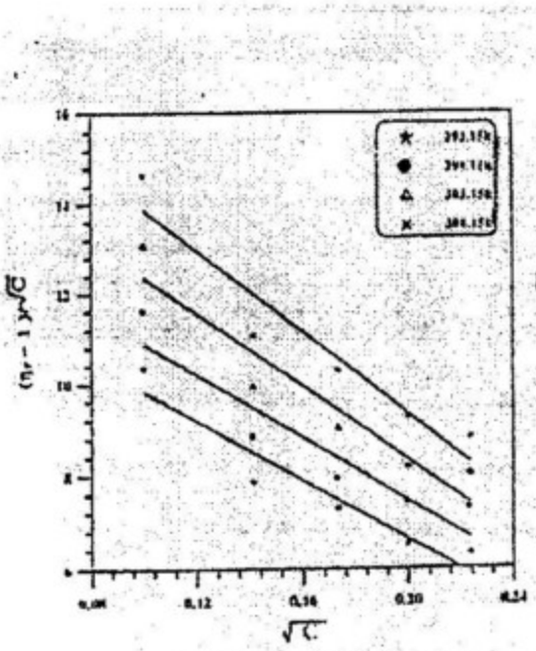
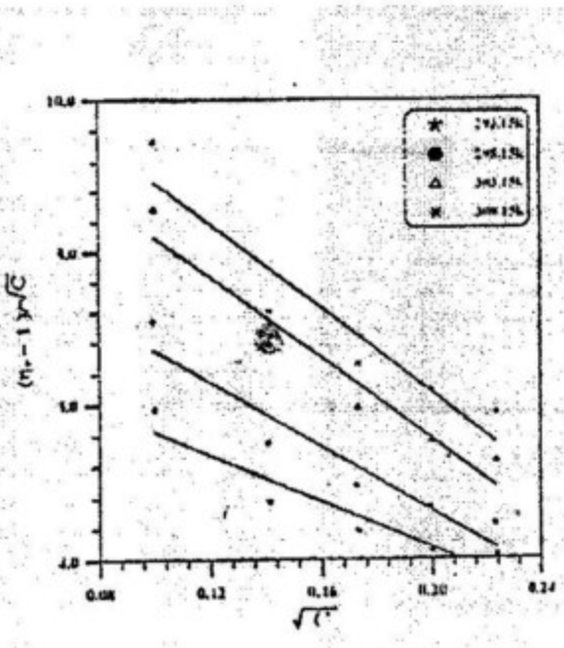


Fig. 1 b :- apparent molal volume ($\Phi^o v$) for B_3 a(298) ,b(303) ,c(308) k



(a)
Vitamin B1



(b)
Vitamin B3

Fig .2 :- $(\eta_r - 1) / \sqrt{c}$ values versus $\sqrt{c}$ for B_1 and B_3 at different temperature (293 – 308) K .

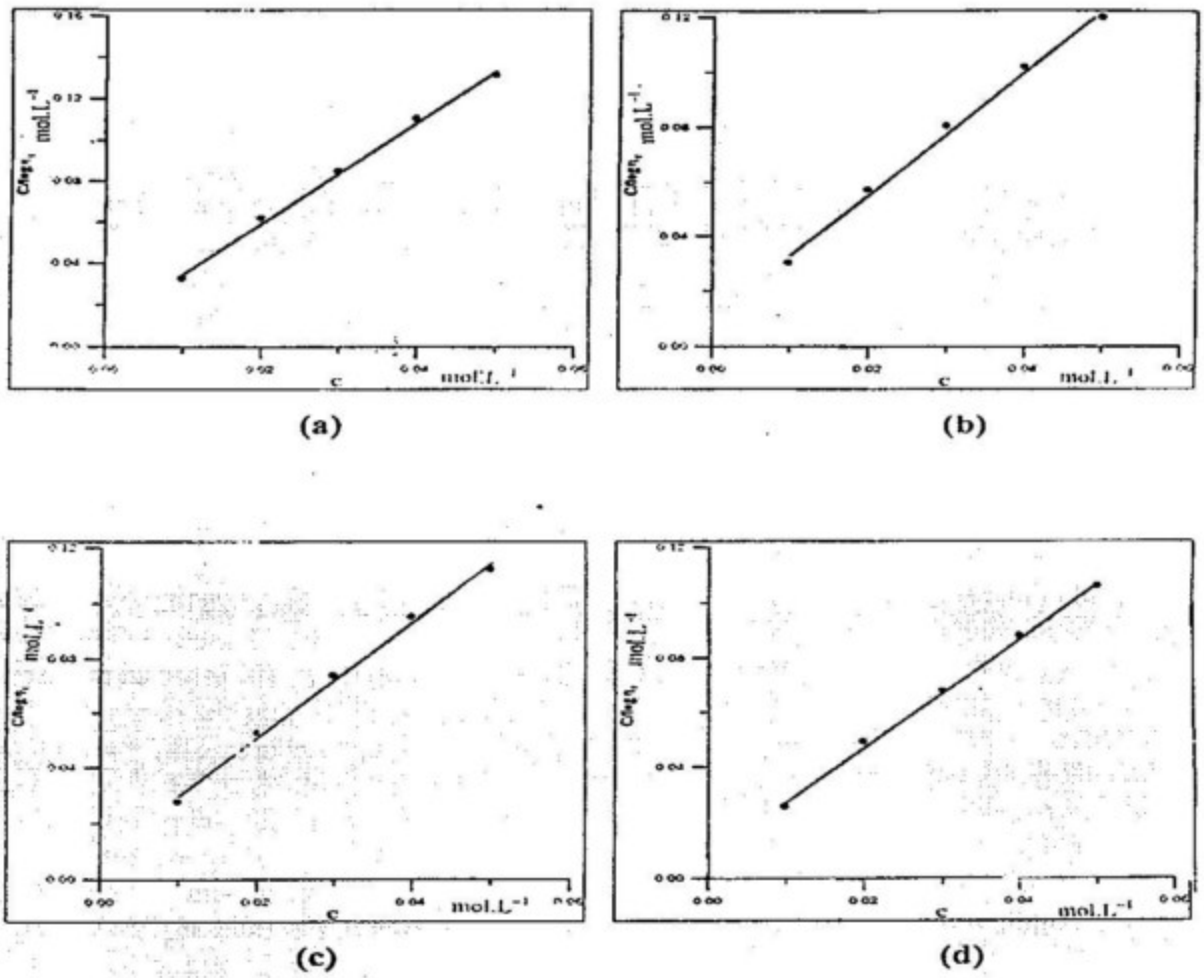


Fig 3.a :- c/log η_r values versus (c) for B_1 for concentration range (0.01 – 0.05) mol L^{-1} at different temperatures (293-308) K .

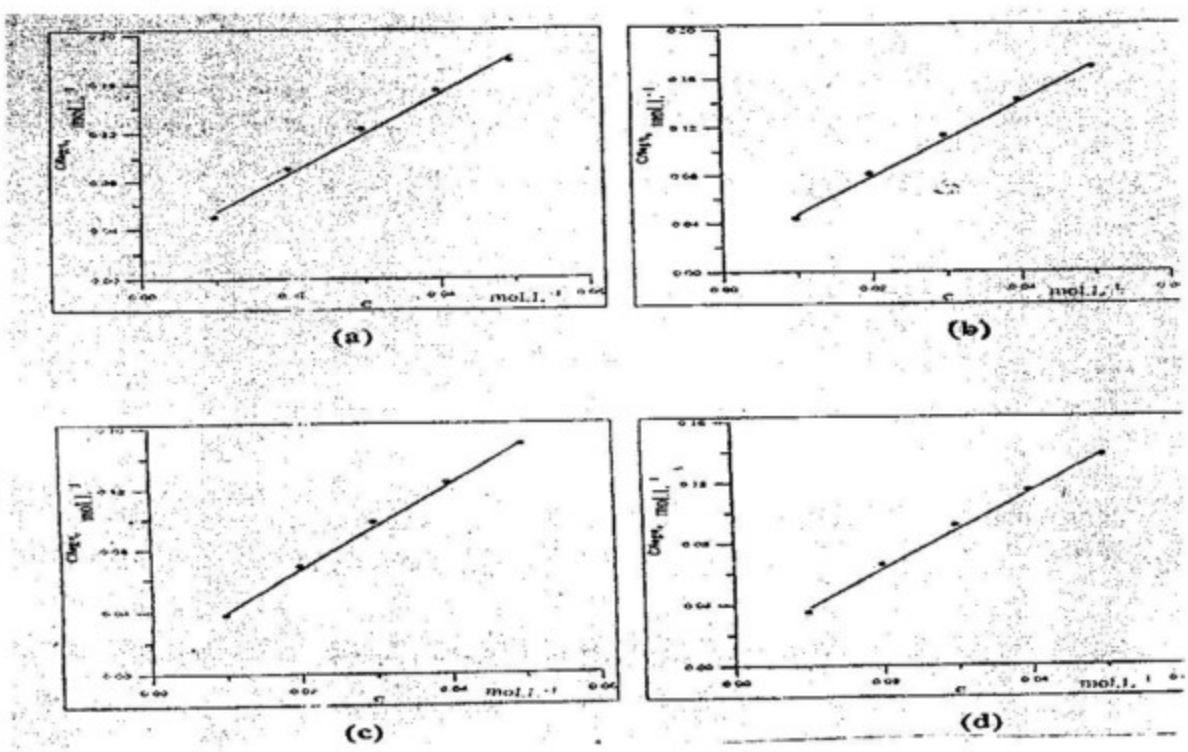


Fig .3.b :- c/log η_r values versus (c) for B_3 for concentration range (0.01 –0.05) mol L^{-1} at different temperatures (293-308) K .

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

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الخلاصـة

تم بحث تداخل المذاب- المذيب في هذه الدراسة باستعمال (B_1, B_3) كمذاب والماء كمذيب عند اربع درجات حرارية ، شملت الدراسة الحسابات النظرية للحجم المولالي الجزئي، وحجم فاندرفال وعلاقتها مع بعضها ومقارنتها مع القياسات العملية ومناقشتها.

وتم قياس اللزوجة للمحاليل المختارة وتطبيق معادلة جونز – مول ومناقشتها مع التراكيز ودرجات الحرارة وعلاقتها مع الحجم المولالي الجزئي.