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Studies in Acoustical Properties of Glycyl-Glycyl-Glycine Peptide in 20% Dioxane-Water Mixture at Different Temperatures

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Ultrasonic velocities and densities of glycyl-glycyl-glycine (GGG) peptide in 20% dioxane-water mixture have been evaluated at different temperatures, 298, 303, 308, 313 and 318 K, by using single crystal interferometer at a frequency of 20 MHz. The ultrasonic velocity, density and concentration were used to calculate (i) partial molal volume ϕ_v, (ii) adiabatic compressibility β_s, (iii) Apparent molal compressibility $\phi_{k(s)}$, (iv) intermolecular free-length L_f, (v) specific acoustic impedance (Z), and (vi) relative association (R_A) through the light on the solute-solvent and solute-solute interaction. It is observed that ϕ_v^o values increase gradually with increase in temparature, but there is no regular order of $\phi_{k(s)}^0$ with respect to temperature. The value of $\phi_{k(s)}^0$ decreases up to 303 K and further that the values of $\phi_{k(s)}^0$ increase gradually. The data of ϕ_v^0 at different temperatures are used to determine that thermodynamic parameters such as free energy ΔG, enthalpy ΔH and entropy ΔS for glycyl-glycyl-glycine in 20% dioxane-water mixture. The values of ΔG, ΔH, ΔS are found to be 3928.4 calories, 8311.22 calories and 278.88 calories respectively. The value of $\Delta G < 0$ and the value of $\Delta S > 0$ indicate the spontaneous process (*i.e.*, forward direction process.)

Key Words: Acoustical, Properties, Glycyl-glycyl-glycine, Peptide, Dioxane-water.

INTRODUCTION

Ultrasonic wave propagation in liquids has been the subject of exhaustive research. Pasynki[1] in 1938 has drawn the conclusion from adiabatic compressibility studies of aqueous electrolyte solutions that the structure of water becomes more highly co-ordinated and compacted with the introduction of ions. Compressibility and apparent molal volumes of many electrolytes in mixed organic solvents were found out by Arrhenius[2]. Sound velocity is a thermodynamic function from which other thermodynamic properties of electrolytic solutions are determined[3–5]. In recent years ultrasonic velocity studies in many of the aqueous and non-aqueous electrolytic solutions have led to a new insight into the process of ion-ion and ion-solvent interactions. Upadhyay *et al.*[6] have studied partial

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molal volumes of kx-glucose solution and verified Young's rule for non-electrolyte systems. The sound velocity and isotropic compressibilities of 1-2-dichloroethane with isometric and branched alcohols have been determined by Rambabu *et al.*[7] Wadi and Goyal[8] have determined limiting apparent molal volumes $\phi_v{}^o$, solvation number S_n of electrolytes in aqueous medium. Effects of substituents on the interaction of some phenols and thiophenols with ketones and nitrobenzene through ultrasonic measurments have been studied by Gnanasekaran and Alamelu[9]. Acoustical properties of glycyl-glycyl-glycine peptide in 20% dioxane-water mixure and 20% methanol-water mixure have been studied by Sondawale *et al.*[10]

EXPERIMENTAL

Glycyl-glycyl-glycine peptide was crystallized from hot water and its purity was checked by melting point and IR spectra. Vogel's standard method was applied for purification of methanol and double distilled water was used to prepare solutions of different concentrations of peptide and mixed with purified methanol. A pyknometer mounted in temperature controlled bath at 25–35°C to an accuracy of ±0.01°C was used for density measurements. The maximum uncertainty in density reading was ±0.00005 units. The velocities of ultrasonic waves of frequency 2.0 MHz were measured by M-82 interferometer instrument for all different concentrations of peptide in 20% dioxane-water mixture.

RESULTS AND DISCUSSION

In the present investigation, different thermodynamic parameters such as adiabatic compressibility (β_s), apparent molal compressibility (ϕ_{ks}), apparent molal volumes (ϕ_v), intemolecular free length (L_f), specific acoustic impedance (Z) and relative association (R_A) have been calculated in 20% dioxane-water mixture, with the help of the following equations:

$$\beta_s = \frac{100}{U_s{}^2 \times d_s} \quad (1)$$

$$\phi_s = \frac{M}{d_s} + \frac{(d_0 - d_s) \times 10^{-3}}{m_s \times d_s \times C}) \quad (2)$$

$$\phi_{k(s)} = \frac{1000(\beta_s d_0 - \beta_0 d_s)}{m \times d_s d_0} + \frac{\beta_s \times M}{d} \quad (3)$$

$$L_f = K \times \sqrt{\beta_s} \quad (4)$$

$$Z = U_s \times d_s \quad (5)$$

$$R_A = \frac{d_s}{d_0}\left(\frac{U_0}{U_s}\right)^{1/3} \quad (6)$$

where d_s, d_0 and U_s, U_0 are the densities and velocities of solution and solvent respectively. M is molecular weight of solute peptide, β_s and β_0 are the adiabatic compressibilities of solution and solvent respectively, K is Jacobson's constant and m is molality of solution. The variation of ultrasonic velocity in a solution depends on the intermolecular free length on mixing, on the basis of a model for sound propagation proposed by Eyring's and Kincaid[14].

The values of ϕ_v, $\phi_{k(s)}$, β_s, d_s L_f, Z, U_s and R_A obtained in the present investigation at different concentrations are presented in Tables 1 and 6. The studyof ϕ_v and $\phi_{k(s)}$ of glycyl-glycyl-glycine (GGG) in 20% dioxane = water media at different temperatures 298, 303, 308, 313 and 318 K have been studied in the present investigation in 20% dioxane-water media.

It is observed that the intermolecular free length (L_f), relative association (R_A) and specific acoustic impedence (Z) are evaluated as shown in Tables 1(a)–5(a) and 1(b)–5(b).

TABLE-1(a)

System: GGG; Medium: 20% dioxane-water; Ultrasonic frequency: 2 MHz; Ultrasonic velocities (U_s), densities (d_s), adiabatic compressibilities (β_s) at different concentrations of peptide in 20% D-W mixture at 298 K.

Concentration of peptide mole L^{-1} (m)	Ultrasonic velocity U_s (m/s)	Density d_s (g cm^{-3})	Adiabatic compepressibility β_s (bar^{-1})	Interamolecular free length L_f (Å)
4.0×10^{-4}	1558.79	1.0195	4.0368 × 10–5	3.8239×10^{-2}
6.0×10^{-4}	1556.44	1.0185	4.0529 × 10–5	3.8315×10^{-2}
8.0×10^{-4}	1559.44	1.0157	4.0485 × 10–5	3.8295×10^{-2}
10.0×10^{-4}	1559.33	1.0164	4.0463 × 10–5	3.8284×10^{-2}

$d_0 = 1.0238$ (in 20% D-W), $U_0 = 1565.20$, $\beta_0 = 3.9869 \times 10^{-5}$

TABLE-1(b)

System: GGG; Medium: 20% dioxane-water; Ultrasonic frequency = 2 MHz; Temp. = 298 K. Apparent molal volume ϕ_v, Apparent adiabatic compressibility $\phi_{k(s)}$, Specific accoustic impedance (Z), Relative association (R_A) in different concentraion of peptide in 20% D-W mixture at 298 K.

Concentration of peptide [mol L^{-1}]	v_m	Apparent molar volume (cm^3 mol^{-1})	Apparent adiabatic compressibility, $\phi_{k(s)}$	Relative association (R_A)	Pecific accoustic impedance, $\times 10^{-4}$ (m s^{-1} g cm^{-3})
4.0×10^{-4}	0.020	186.4212	2.6440	0.9950	0.1583
6.0×10^{-4}	0.0244	185.7717	1.4252	0.9966	0.1585
8.0×10^{-4}	0.0282	186.2851	1.1537	0.9933	0.1583
10.0×10^{-4}	0.0314	186.8586	83.8498	0.9946	0.1584

It could seen from the tables that intermolecular free length (L_f) decreases linearly on increasing the concentration of peptide solution and hence there is increase in ultrasonic velocities with concentration of peptide. This indicates that there is a significant interaction between ion and solvent molecules, suggesting a structure promoting behaviour of the added electrolyte. This may also imply a decrease in the number of free ions, showing the occurrence of ionic association due to strong ion-ion interaction. It is also observed from Tables 1(a)–5(a) and 1(b)–5(b) that there is a linear variation of relative association (R_A) and specific acoustic impendence (Z) values with respect to the concentration of the solution. The lower values of R_A signify a weak association between solute and solvent.

TABLE-2(a)

System: GGG; Ultrasonic frequency = 2 MHz; Temp = 303 K; Ultrasonic velocities (U_s), densities (d_s), adiabatic compressibilies (β_s) at different concentrations of peptide in 20% dioxane-water mixure.

Concentration of peptide [mol L^{-1}]	Ultrasonic velocity (m/s)	Density (g cm^{-3})	Adiabatic compressibility (bar–1)	Interamolecular free length (Å)
2×10^{-4}	1560.01	1.0150	4.1313×10^{-5}	3.868×10^{2}
4×10^{-4}	1561.30	1.0157	4.1194×10^{-5}	3.863×10^{2}
6×10^{-4}	1561.80	1.0162	4.0606×10^{-5}	3.834×10^{2}
8×10^{-4}	1562.26	1.0169	4.0455×10^{-5}	3.810×10^{2}
10×10^{-4}	1550.80	1.0153	4.1295×10^{-5}	3.869×10^{2}
12×10^{-4}	1565.02	1.0178	4.0068×10^{-5}	3.807×10^{2}

$d_0 = 1.0234$ g cm^{-3}; $U_0 = 1566.33$ m s^{-1}; M = 189.2 g; K = Jacobson's constant (6.0186×10^{-4} at 303 K)

TABLE-2(b)

System: GGG; Ultrasonic frequency = 2 MHz; Temp = 303 K; Apparent molal volume ϕ_v, Apparent adiabatic compressibility $\phi_{k(s)}$, Specific accoustic impendence (Z), Relative association (R_A) in different concentraions.

Concentration of peptide [mol L^{-1}]	Apparent molar volume (cm^3 mol^{-1} ϕ_v)	Apparent adiabatic compressibility, $\phi_{k(s)}$	Relative association	Pecific accoustic impedence $\times 10^{-4}$ (m s^{-1} g cm^{-3})
2.0×10^{-4}	185.7011	1.6305	0.9935	0.1583
4.0×10^{-4}	186.1953	1.5435	0.9933	0.1585
6.0×10^{-4}	186.3219	1.3449	0.9988	0.1587
8.0×10^{-4}	186.7924	1.0945	0.9936	0.1588
10.0×10^{-4}	187.0052	1.0829	0.9943	0.1574
12.0×10^{-4}	185.8955	0.3834	0.9945	0.1589

TABLE-2(c)

ϕ_v AND $\phi_{k(s)}$ VALUES OF GGG IN 20% D-W MIXTURE

System	Medium	$\phi_{k(s)}$	ϕ_v^0
GGG	D-W	1.95	184.95

TABLE-3(a)

System: GGG; Medium: 20% dioxane-water; Ultrasonic frequency = 2 MHz; Temp. = 308 K; Ultrasonic velocities (U_s), densities (d_s), adiabatic compressibilies (β_s) at differ ent concentrations of peptide in 20% D-W mixture at 308 K.

Concentration of peptide [mol L^{-1}]	Ulrasonic velocity (m/s)	Density (g cm^{-3})	Diabatic compressibility (bar^{-1})	Interamolecular free length (Å)
2.0×10^{-4}	1565.46	1.0125	4.0301×10^{-5}	3.8207×10^{2}
4.0×10^{-4}	1560.98	1.0172	4.0345×10^{-5}	3.8228×10^{2}
6.0×10^{-4}	1569.11	1.0153	4.0003×10^{-5}	3.8066×10^{2}
8.0×10^{-4}	1558.95	1.0140	4.9563×10^{-5}	3.7856×10^{2}
10.0×10^{-4}	1561.55	1.0136	4.0459×10^{-5}	3.8282×10^{2}
12.0×10^{-4}	1566.27	1.0145	4.0480×10^{-5}	3.8150×10^{2}

$U_0 = 1568.20$, $d_0 = 1.0230$ (in 20% D-W), $\beta_0 = 3.9748 \times 10^{-5}$

TABLE-3(b)

System: GGG; Ultrasonic frequency = 2 MHz; Medium: 20% dioxane-water; Temp. = 308 K; Apparent molal volume ϕ_v, Apparent adiabatic compressibility $\phi_{k(s)}$, Specific accoustic impendance (Z), Relative association (R_A) in different concentraion of peptide in 20% D-W mixture at 308 K

Concentration (m)	V_m	Apparent molar volume (cm^3 mol^{-1})	Apparent adiabatic compressibility $\phi_{k(s)}$	Relative association	Specific accoustic impedence $\times 10^{-4}$ (m s^{-1} g cm^{-3})
2.0×10^{-4}	0.0141	186.9147	4.7531	0.9903	0.1585
4.0×10^{-4}	0.0200	186.0146	2.0286	0.9958	0.1587
6.0×10^{-4}	0.0244	186.3611	0.9171	0.9922	0.1593
8.0×10^{-4}	0.0282	186.5985	0.2103	0.9931	0.1580
10.0×10^{-4}	0.0314	187.4818	1.0692	0.9898	0.1582.
12.0×10^{-4}	0.0346	187.1785	62.6411	0.9920	0.1588

TABLE-4(a)

System: GGG; Medium: 20% dioxane-water; Ultrasonic frequency = 2 MHz; Temp = 313 K. Ultrasonic velocities (U_s), densities (d_s), adiabatic compressibilies (β_s) at different concentration of peptide in 20% D-W mixture at 313 K.

Concentration of peptide [mol L^{-1}]	Ultrasonic velocity (m/s)	Density (g cm^{-3})	Adiabatic compressibility (bar^{-1})	Interamolecular free length (Å)
4.0×10^{-4}	1561.30	1.0163	4.0365×10^{-5}	3.8238×10^{2}
6.0×10^{-4}	1559.76	1.0157	4.0468×10^{-5}	3.8287×10^{2}
8.0×10^{-4}	1564.19	1.0144	4.0291×10^{-5}	3.8203×10^{2}
10.0×10^{-4}	1561.55	1.0121	4.0519×10^{-5}	3.8311×10^{2}
12.0×10^{-4}	1599.08	1.0135	4.0229×10^{-5}	3.8173×10^{2}

$d_0 = 1.0226$ (in 20%D-W), $U_0 = 1569.5$, $\beta_0 = 3.9969 \times 10^{-5}$

TABLE-4(b)

System: GGG; Medium: 20% dioxane-water; Ultrasonic frequency = 2 MHz; Temp. = 313 K; Apparent molal volume ϕ_v, Apparent adiabatic compressibility $\phi_{k(s)}$; Specific acoustic impedance (Z), Relative association (R_A) in different concentration of peptide in 20% D-W mixture at 313 K

Concentration (m)	V_m	Apparent molar volume ($cm^3\ mol^{-1}$)	Apparent adiabatic compressibility $\phi_{k(s)}$	Relative association	Specific acoustic impedance × 10^{-4} ($m\ s^{-1}\ g\ cm^{-3}$)
4.0×10^{-4}	0.0200	186.1806	2.2527	0.9955	0.1586
6.0×10^{-4}	0.0244	186.2864	1.7105	0.9953	0.1584
8.0×10^{-4}	0.0282	186.5239	1.1 305	0.9931	0.1586
10.0×10^{-4}	0.0314	187.9534	121.4990	0.9914	0.1580
12.0×10^{-4}	0.0346	187.4118	72.7548	0.9918	0.1587

TABLE-5(a)

System: GGG; Medium: 20% dioxane-water; Ultrasonic frequency = 2 MHz; Temp. = 318 K. Ultrasonic velocities (U_s), densities (d_s), adiabatic compressibilies (β_s) at different concentrations of peptide in 20% D-W mixure at 318 K.

Concentration of peptide [mol L^{-1}]	Ultrasonic velocity (m/s)	Density ($g\ cm^{-3}$)	Adiabatic compressibility (bar^{-1})	Interamolecular free length (Å)
4.0×10^{-4}	1560.38	1.0150	4.0464×10^{-5}	3.8385×10^{2}
6.0×10^{-4}	1563.10	1.0143	4.0351×10^{-5}	3.8231×10^{2}
8.0×10^{-4}	1563.93	1.0138	4.0328×10^{-5}	3.8220×10^{2}
10.0×10^{-4}	1564.30	1.0111	4.0417×10^{-5}	3.8263×10^{2}
12.0×10^{-4}	1565.13	1.0123	4.0326×10^{-5}	3.8219×10^{2}

$d_0 = 1.0222$ (in 20% D-W), $U_0 = 1570.30$; $\beta_0 = 3.9673 \times 10^{-5}$

TABLE-5(b)

System: GGG; Medium: 20% dioxane-water; Ultrasonic frequency = 2 MHz; Temp = 318 K; Apparent molal volume ϕ_v, Apparent adiabatic compressibility $\phi_{k(s)}$, Specific accoustic impendence (Z), Relative association (R_A) in different concentration of D-W mixture at 318 K

Concentration (m)	V_m	Apparent molar volume ($cm^3\ mol^{-1}$)	Apparent adiabatic compressibility, $\phi_{k(s)}$	Relative association	Specific accoustic impedance × 10^{-4} ($m\ s^{-1}\ g\ cm^{-3}$)
4.0×10^{-4}	0.0200	186.4212	2.6440	0.9950	0.1583
6.0×10^{-4}	0.0244	186.5451	1.6252	–	–
8.0×10^{-4}	0.0282	186.6346	1.2169	0.9931	0,1585
10.0×10^{-4}	0.0314	188.1974	116.2514	–	–
12.0×10^{-4}	0.0346	187.0252	85.4426	0.9914	0.1584

The plots between $\phi_v/\phi_{k(s)}$ and concentration $\sqrt{m}$ are shown in Figs. 1 to 10. The plots between $\phi_{k(s)}$ and $\sqrt{m}$ showed linear relationship up to the concentration 8×10^{-4} M are shown in Figs. 2, 4, 6, 8 and 10. The plots between ϕ_v and $\sqrt{m}$ show the linear relationships in Figs. 1, 3, 5, 7 and 9.

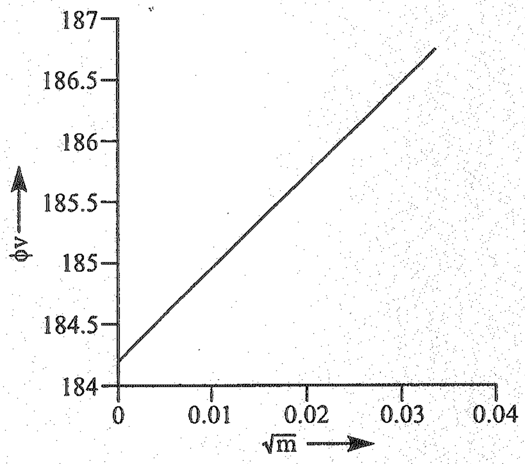

Fig. 1. Plot between $\phi_v/\phi_{k(s)}$ *vs.* $\sqrt{m}$ (system: GGG; medium: 20% D-W; temperature = 298 K; $\phi_v{}^0 = 184.2$)

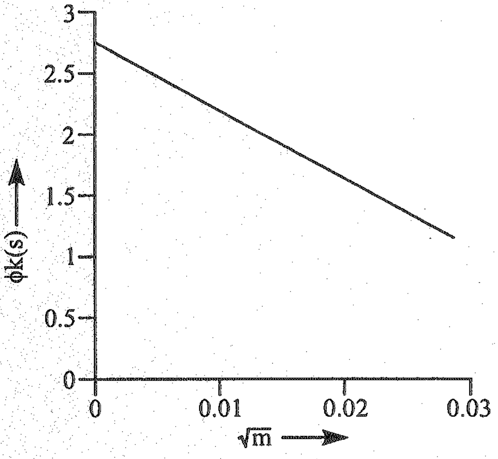

Fig. 2. Plot between $\phi_v/\phi_{k(s)}$ *vs.* $\sqrt{m}$ (system: GGG; medium: 20% D-W; temperature = 298 K; $\phi_{k(s)}{}^0 = 2.75$)

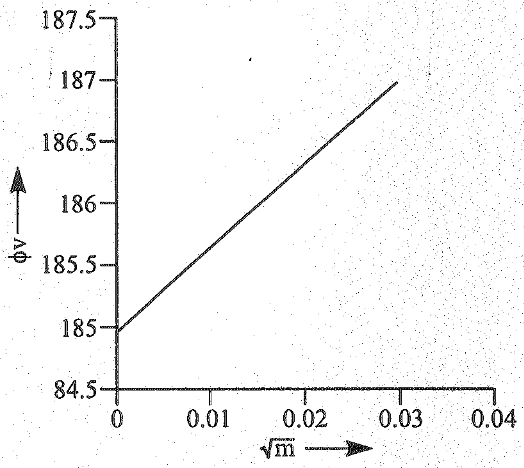

Fig. 3. Plot between $\phi_v/\phi_{k(s)}$ *vs.* $\sqrt{m}$ (system: GGG; medium: 20% D-W; temperature = 303 K; $\phi_v{}^0 = 184.95$)

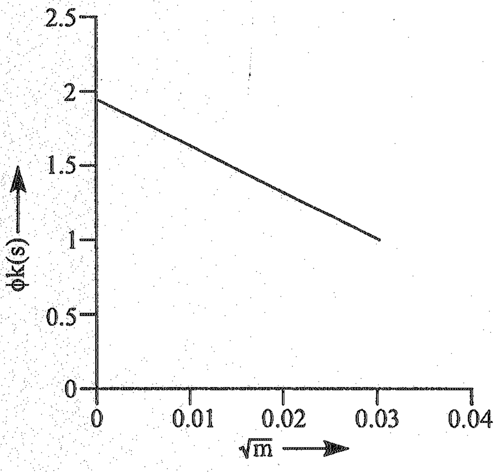

Fig. 4. Plot between $\phi_v/\phi_{k(s)}$ *vs.* $\sqrt{m}$ (system: GGG; medium: 20% D-W; temperature = 303 K; $\phi_{k(s)}{}^0 = 1.95$)

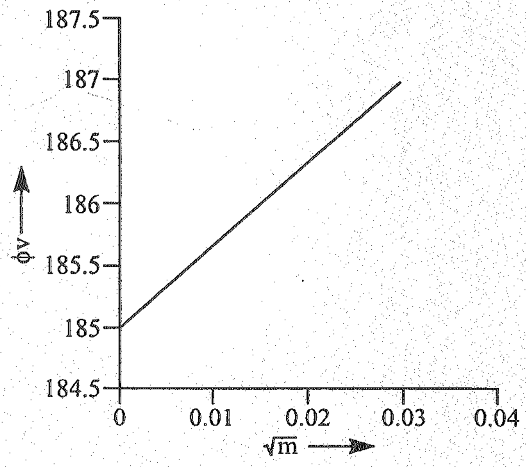

Fig. 5. Plot between $\phi_v/\phi_{k(s)}$ *vs.* $\sqrt{m}$ (system: GGG; medium: 20% D-W; temperature = 308 K; $\phi_v{}^0 = 185.0$)

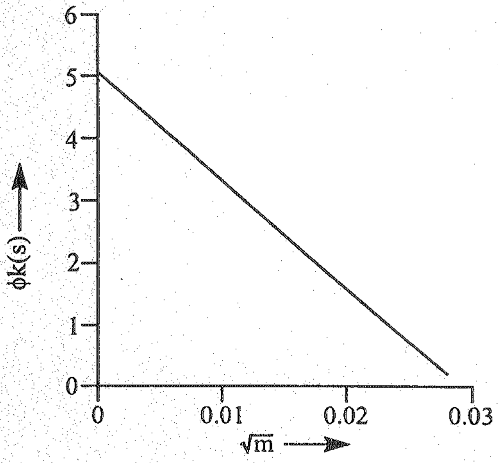

Fig. 6. Plot between $\phi_v/\phi_{k(s)}$ *vs.* $\sqrt{m}$ (system: GGG; medium: 20% D-W; temperature = 308 K; $\phi_{k(s)}{}^0 = 5.1$)

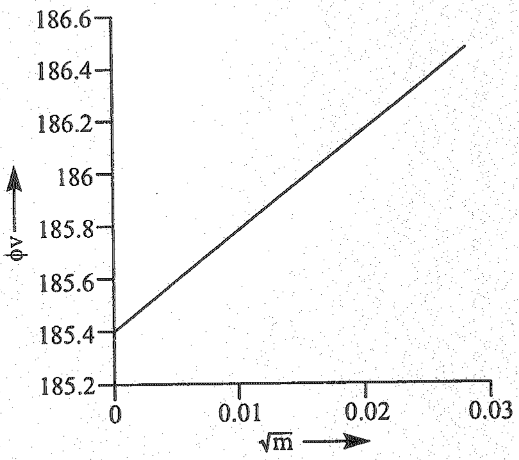

Fig. 7. Plot between $\phi_v/\phi_{k(s)}$ *vs.* $\sqrt{m}$ (system: GGG; medium: 20% D-W; temperature = 313 K; $\phi_v^0 = 185.4$)

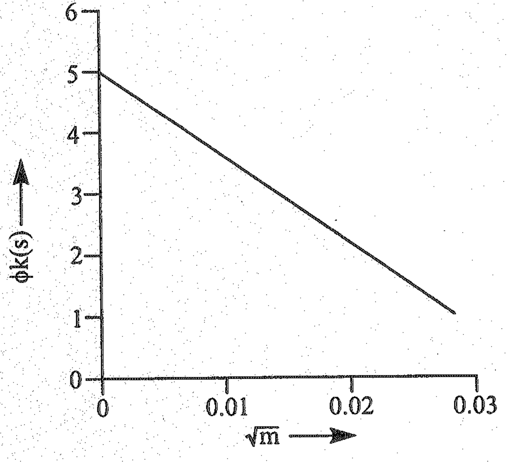

Fig. 8. Plot between $\phi_v/\phi_{k(s)}$ *vs.* $\sqrt{m}$ (system: GGG; medium: 20% D-W; temperature = 313 K; $\phi_{k(s)}^0 = 5.0$)

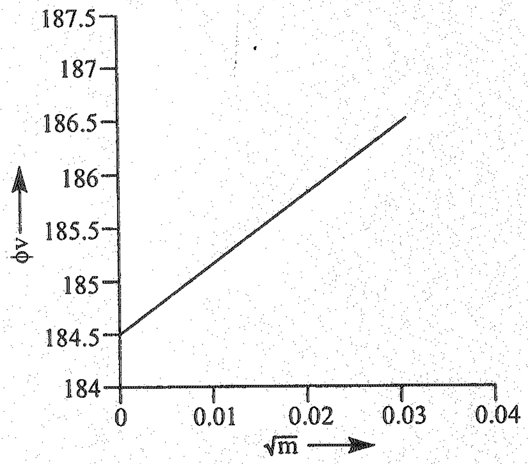

Fig. 9. Plot between $\phi_v/\phi_{k(s)}$ *vs.* $\sqrt{m}$ (system: GGG; medium: 20% D-W; temperature = 318 K; $\phi_v^0 = 184.45$)

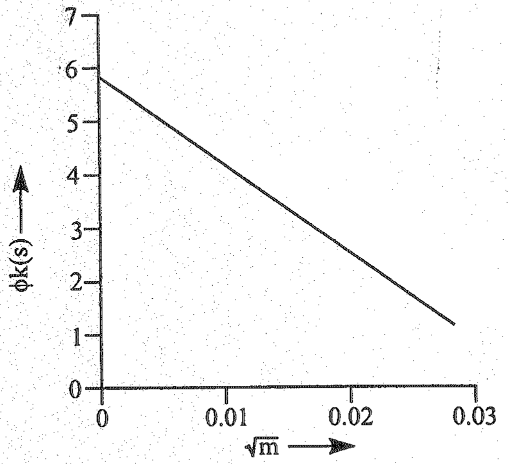

Fig. 10. Plot between $\phi_v/\phi_{k(s)}$ *vs.* $\sqrt{m}$ (system: GGG; medium: 20% D-W; temperature = 318 K; $\phi_{k(s)}^0 = 5.85$)

The data obtained of ϕ_v^0 and $\phi_{k(s)}^0$ with respect to temperature are presented in Table-6.

TABLE-6
THE VALUES OF ϕ_v^0 AND $\phi_{k(s)}^0$ OF GLYCYL-GLYCYL-GIYCINE AT DIFFERENT TEMPERATURES

Temp. (K)	ϕ_v^0 (cm^3 mol^{-1})	$\phi_{k(s)}^0$ (cm3 mol^{-1} bar^{-1})
398	184.20	2.75
303	184.95	1.95
308	185.00	5.10
313	185.40	5.00
318	184.45	5.85

It is found from the above table that ϕ_v^o values increase gradually with increase in temparature but there is no regular order of $\phi_{k(s)}^o$ with respect to temperature. The value of $\phi_{k(s)}^o$ decreases up to 303 K and further the values of $\phi_{k(s)}^o$ increase gradually. The data of ϕ_v^o at different temperatures are used to determine the thermodynamic parameters such as free energy ΔG, enthalpy ΔH and entropy ΔS for glycyl-glycyl-glycine in 20% dioxane-water mixture. The values of ΔG, ΔH, ΔS are found to be 3928.4, 8311.22 and 278.88 cal respectively. The value of $\Delta G < 0$ and the value of $\Delta S > 0$ indicate the spontaneous process (*i.e.*, forward direction process).

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