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Contents

Molecular Interaction studies of ternary liquid mixtures of 4-methyl-2- Pentanone with cyclohexane and n-pentanol

*YATENDRA KUMAR GUPTA, AVNISH **

ABSTRACT -

Ultra sound velocity, density and viscosity in, ternary liquid mixtures of 4-methyl 2-pentanone with cyclo hexanol and n-pentanol has been determined at 303 k, 308 k, and 313 k over the entire composition range, from the measured parameters, Isentropic compressibility (β_S) inter molecular free length (L_f) Molar volume (V_m) and their excess values have been computed. The excess isentropic and intermolecular free-Length ternary mixtures exhibit negative deviations while excess viscosity and molar volume exhibit positive deviations from ideal behaviour the entire mole fraction.

INTRODUCTION :

The experiment specifies will be discussed in terms of molecular interaction between unlike molecular of the ternary non-aqueous system. These may be attributed to the change in the adhesive and cohesive for us[1]. The dispersion forces may contribute to positive deviations where the sizes of molecules are taken in consideration. The negative deviations, which are strikingly large in magnitude indicate complex formation between unlike molecules of the mixtures Gill et. al[2] investigated ultrasound velocity, density, viscosity of ternary mixtures of benzenitrile with methanol, acetone, acetonitrile, dimethyl formide, pyridine, dimethyl, sulphoxide and carbon tetra chloride at 298 k. Rai et al[3] measured excess properties of non aqueous ternary system ultrasonically of hydrocarbon mixtures and tested flory theory at 298.15 k .

The present investigation deals with study of the excess molar volume (V_m^E) and excess viscosity (η^E). For the ternary liquid mixtures 4-methyl-2-pentanone with cyclo hexanol and pentanol at 303 k , 308 k, and 313 k . These systems are typical ternary mixtures with a wide scope for complexation through hydrogen bonding.

EXPERIMENTAL DETAILS :

All the liquids used in the present study have been distilled to remove impurities following standard procedures. The Purity of each sample was checked by comparing the measured density of component with these reported in the literature.[4] Ultrasound

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velocities were measured using single crystal ultrasound interferometer of 2 MHz frequency and the data were accurate up to 0.2 %. Densities of the mixtures have been determined by using by pkynometer and electric balance. The viscosities have been determined by using ostwald viscometer. The tempratures were maintained by circulating water around liquid cell from a thermostate controlled at 303 k, 308 k, and 313k.

The value of β_s were calculated using the relation $\rightarrow \beta_s = \rho^{-1}v^{-2}$

Intermolecular free length (L_f) has been calculated using the formula –

$$Lf = k(\beta_s)^{1/2}$$

Where : k is the jacobson's [5] constant V_m is the molar volume calculated by following formula–

$$V_m = \overline{M}/\rho$$

Where : $\overline{M} = X_1M_1 + X_2M_2 + X_3M_3$,

ρ is the experimental densities X_1, X_2 and X_3 are mole fraction of component 1, 2 and 3, M_1, M_2, M_3 are the molecular weight of component 1, 2 and 3 and its $\rightarrow$

$$V_m^E = V_m \exp - [X_1V_{A_1} + X_2V_{A_2} + X_3V_{A_3}]$$

Excess value have been calculated by using formula –

$$\beta_s^E = \beta_s \exp - (X_1\beta s_1 + X_2\beta s_2 + X_3\beta s_3)$$

$$L_f^E = L_f \exp - (X_1Lf_1 + X_2Lf_2 + X_3Lf_3)$$

Excess viscosity has been calculated by using formula –

$$\eta^E = \eta \exp - (X_1\eta_1 + X_2\eta_2 + X_3\eta_3)$$

RESULTS AND DISCUSSION :

The value of ultrasound velocity, density, viscosity, excess compressibility, excess inter molecular free length (L_f^E), excess molar volume (V_m^E) are represented in table (1-3) and there excess parameters β_s^E, V_m^E, L_f^E and η^E mole fraction curves are also ploted in figure (1-4)

Mole fraction (X_1) of 4-methyl 2- pentanone, (X_2) mole fraction of cyclo hexane, density, ultrasound velocity (v), viscosity (η), excess viscosity (ηE), excess isentropic compressibility (β_s^E), excess inter molecular free length (L_f^E) and excess molar volume (V_m^E) for the ternary liquid mixture at 303 k, 308 k, 313 k.

Table 1 -- 4-methyl 2-pentanone + cyclo hexane + n- pentanol at 303 k

X_1	X_2	ρ	v	η	η^E	β_s^E	L_f^E	V_m^E
00	00	0.8075	1238	3.0300	0.000	0.000	0.000	0.000
0.00	1.00	0.7628	1252	0.7692	0.00	0.00	0.000	0.00
0.00	0.60	0.7722	1257	1.8288	0.1553	-0.56	-0.0019	2.00

0.10	D.50	0.7789	1264	1.9156	0.2658	-1.35	-0.0048	1.60
0.20	D.40	0.7819	1274	1.9640	0.3379	-02.08	-0.0075	1.43
0.30	D.30	0.7889	1281	1.9916	0.3892	-2.81	-0.0104	1.03
0.40	D.20	0.7916	1287	1.9747	0.3959	-2.97	-0.0112	0.88
0.50	D.10	0.7956	1289	1.8899	0.3348	-3.35	-0.0106	0.65
0.60	0.00	0.7981	1292	1.7353	0.2039	-2.04	-0.0073	0.51
1.00	0.00	0.7842	1300	0.5324	0.0000	-0.000	-0.00	0.00

Studied for the ternary mixture of 4-methyl-2-pentanone + cyclo hexane + pentanol at- 303 K, 308K, and 313K.

Table 2 -- 4-methyl 2-pentanone + cyclo hexane + n- pentanol at 308 k

X_1	X_2	ν	ρ	η	η^E	β_s^E	L_f^E	ν_m^E
0.00	0.00	1218	0.8025	2.6850	0.000	0.00	0.000	0.00
0.00	1.00	1232	0.7598	0.7238	0.00	0.00	0.00	0.00
0.00	0.60	1245	0.7648	1.6354	0.1272	-1.27	-0.0043	2.17
0.10	0.50	1254	0.7669	1.6846	0.168	-1.97	-.0064	2.04
0.20	0.40	1261	0.7684	1.7163	0.2490	-2.37	-0.0079	1.95
0.30	0.30	1269	0.7692	1.7269	0.2800	-2.69	-0.0092	1.90
0.40	0.20	1272	0.7701	1.7014	0.2750	-2.43	-0.0084	1.85
0.50	0.10	1275	0.7721	1.6439	0.2380	-2.28	-0.0079	1.73
0.60	0.00	1277	0.7738	1.5441	0.1586	-1.97	-0.0068	1.63
1.00	3.00	1285	0.7630	0.5192	0.000	0.00	0.00	0.00

The excess-values of isentropic compressibility and intermolecular free length both are negative while excess molar volume and excess viscosity are positive in the table 1, 2 and 3 and also excess values. graph shown in the figure 1, 2 and 3.

Table 3 -- 4-methyl 2-pentanone + cyclo hexane + n- pentanol at 313 k

X_1	X_2	ν	ρ	η	η^E	β_s^E	L_f^E	ν_m^E
0.00	0.00	0.7993	1198	2.3400	0.00	0.00	0.00	0.00
0.00	1.0	0.7568	1213	0.6972	0.00	0.00	0.00	0.00
0.00	0.60	0.7616	1220	1.4124	0.0581	-0.53	-0.0018	2.18
0.10	0.50	0.7647	1226	1.4367	0.1025	-1.06	-0.0037	2.00
0.20	0.40	0.7668	1232	1.4594	0.1452	-1.46	-0.0050	1.87
0.30	D.30	0.7784	1237	1.4782	0.1840	-1.64	-0.0057	1.77
0.40	0.20	0.7718	1242	1.4861	0.2120	-2.01	-0.0069	1.57
0.50	o.io	0.7732	1247	1.4555	0.2014	-2.15	-0.0075	1.49
0.60	0.5.00	0.7751	1249	1.3770	0.1430	-1.93	-0.0067	1.38
1.00	0.00	0.7606	1250	0.4968	0.0000	00000	0,000	0,000

Deviation of theoretical values of velocity from the experimental values is attributed to the presence of inter molecular interaction in the systems studied. It may be concluded that out of three theories and relations Nemoto relations is best.

Singh and sexena[6] deliberate the ternary liquid mixtures of butly acetate ethyl acetate phenol and n -butyl alcohol in carbon tetra chloride using di electric techniques, at micro frequencies. Gill et al [7] investigated ultrasound velocity, density and viscosity of ternary liquid mixtures of benzenitrile with methanal, acetone, acetone nitrile, dimethyl formide, pyridine, dimethyl sulphoxide and carbon tetra chloride at 298 k and the results agreed with the present work.

CONCLUSION :

The new measurements of density (ρ) viscosity (η) and ultrasound velocity at 303k, 308 k and 313 k are reported for 4-methyl 2-pentanone cyclo hexane and pentanol ternary liquid muxture in the present work. It has been observed that positive deviations of excess velocity, excess internal pressure, excess Gibb's energy, whereas negative deviations were observed for excess free volume at 303k, 308k and 313k.

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Laboratory Study on the Insecticidal Property Azadirachta Indica and Zingerber Officinale on Trichoplusia ni

ESHENDRA KUMAR AND SHAILENDRA KUMAR***

INTRODUCTION:

Trichoplusia ni is belongs to the family Noctldiae of order lepidoptera, has a great economic importance. Many vegetables crops such as Brassia Oleracea var botrytis, collards brocoloi, some times tomato and cucumber too damaged by Trihoplusia ni. Field crops which are also attacked by Trichoplusia ni are Cotton and Soyabeen. Collards and Cotton are most preferred host for egg laying. The United Nations Conference on Environment and Development (UNCED) held in Rio de Janeiro (1992) prepared Agenda, to which stresses the need to increase the use of integrated pest, disease and crop management techniques to eliminate over dependence on agrochemical thereby encouraging environmentally sustainable agricultural practices. Recent awareness about the hazards of persistant synthetic pesticides and their high cost have generated fresh interest and intensified research on pesticides of plant origin.

MATERIALS AND METHODS:

Seeds of Azadiracta indica and dried rizoms of Zingerber officinale, were purchased from local market, dried in oven at 80°C and grinded into powder using hand grinder. Extraction were done in a Soxhlet's apparatus with methanol use as a solvent. The material extracted till the clear solvent was obtained. The left over extract was raised up to the volume of 50 ml. by adding methanol. This was considered as 100% Technical material. The 50 ml. extract was take into the reagent bottle and 50 ml. methanol was added in it this way 50% stock solution was prepared. The 0.50%, 1.00% and 1.50% concentrations were prepared from this stock solution using methanol as solvent trition X-100 as emulsifire.

Adult of Trichoplusia ni were captured from the host crop and cultured in laboratory at 28 - 30°C. They were fed on host leaves. The insecticidal properties of extracts were assessed in laboratory condition by film residue method. Adults boiassays were done in petri dishes (90mm). One ml of each dose was dropped separately, covering (space), uniformly the whole area of petridish. After air dried then adults were released in each

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petridish. Three replications of each treatment were maintained. In each set of extract one control was a separate clean glass jar containing fresh leaves as a food. Mouth of jar was kept closed with cotton clothes. Observation on adult mortility were done after 12 hours. The mortility percentage was corrected using Abbott's formula (Abbott's 1925). The observed data was subjected to Probit analysis (Finney, 1947).

RESULT AND DISCUSSION :

The extracts caused various degree of mortility of the Trichoplusia ni and offer various level of protection. It's clearly seen from the Table 1, that 0.5% concentration of Azadirachta indica extract provided 44.40% mortility of Trichoplusia ni in 0.5% concentration 63.00% mortility in concentraion 1.0% and in 1.5% concentration gave 83.00%. Zingiber officinale extract showed 30.31% mortility in 0.5% concentration, 49.00% in 1.0% concentration and 53.23% mortility in 1.5% concentration and in all set of extract control without spraying shows no mortility of Trichoplusia ni. The calculated LC (50), 95% confidence limits, regression equations, chi-square test result and probability and correlation coefficient of data is shown in Table 2.

Table 1

Effect of methanol extract of selected plants of adults of Trichoplusia ni

Extract	Conc. X10 responded%	Observed responded %	Linear responded %	Log conc X 10	Linear probit	Response
Azadirachata indica	5	44.40	42.3035	0.534	4.243	42.39
	10	63.00	68.0324	1.000	4.864	68.04
	15	83.00	80.0021	1.045	5.214	81.00
Zingiber Officinale	5	30.31	31.2132	0.589	4.150	31.78
	10	49.00	47.2178	1.000	4.562	47.20
	15	53.23	56.1121	1.067	5.012	56.09

The calculated Chi-square value is significant in all experiment at 5% level of significance for 1 degree of freedom and correlation coefficient tests. Zingiber officinale contains a sesquiterpene, zingerone which is responsible for its inhibition effect against banana weevil (Purseglove, 1972). The present experiment showed that Trichoplusia ni mortility was the most in Azadirachta indica extract, where as Zingiber officinale was moderately toxic.

Table 2

LC (50), 95% confidential limits, regression equation, X^2, probability of X^2 and correlation coefficient of the extracts

Extract	LC(50)	95% confidential limit L	U	Regression equation	X^2	P	r
Azadirachata Indica	0458	0.421	0.631	Y = 0.901x+4.53	1.912	0.342	0.91
Zingiber Officinale	1.69	0.821	1.423	Y= 0.508x+4.21	0.492	0.481	0.95

L= lower limit, U≡ upper limit, X^2= Chi-square, P= probability of Chi-square, r=Correletion coefficient Tabulated X^2= 2.941 (df 1, at 5% significance level), Tabulated r = 0.98 on (df 2, at 1% significance level).

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EPR, XRD and Microbial Investigations of Ni (II) Hexahydrocyclotriphosphazenide, (HHCTP)

NIKLANK JAIN, S. S. YADAV** & S. P. S. JADON**

ABSTRACT:

On the basis of mass spectrum, the complex of $(N_3P_3H_2)_3$ with Ni (II) formulated as $\{(N_3P_3H_5)_3\text{-}Ni\}_2$ as dimer. The EPR analysis suggests it's diamagnetic character, which is due to Ni - Ni metallic bonding and P^V reduced to P^{III} state. The XRD studies revealed hexagonal geometry of the complex. The complex is found very effective to Klebsiella gm-ve bacteria and Candida albicans fungi, which causes urinogenital and skin disease in human beings.

INTRODUCTION:

Various complexes of 1, 3, 5 hexachlorotriphosphazene ($NPCl_2$) have been reported[1-7], due to lone pair of electrons on N atom. The complexes of $(NPH_2)_3$, hexahydrocyclotriphosphazene, with metals have not been synthesised till now. The XRD and antibacterial studies of the complex of Ni (II) with $(NPH_2)_3$ prepared, are being presented here with.

EXPERIMENTS:

Aldrich make, doubly distilled chemicals and well cleaned glass wares were used. $(NPCl_2)_3$, $(NPH_2)_3$ and complex with Ni(II) were prepared[8] and estimated as described[9]. EPR and X-ray diffraction spectra were recorded on Various X-E-4 Band spectrometer and PW-1710 Philips X-ray diffractometer using Cu-Kα source of radiation (γ= 1.5406Å)in 2θ range - 10-80° at room temperature respectively.

For the antibacterial studies, first of all the apparatus used were cleaned and sterilized.gm+ve, gm-ve bacteria and fungi collected from Jai Hospital and Research Institute, Agra were grown by incubating at 37°C and using agar-agar pepton media. A media for sterilized petridish were prepared by same process using yeast (0.5 g). NaCl (.38 g) and glucose (0.25 gm.) and divided into six equal parts with a hole at centre for control, A thin layer of grown test organism was coated on the surface of each petridish media

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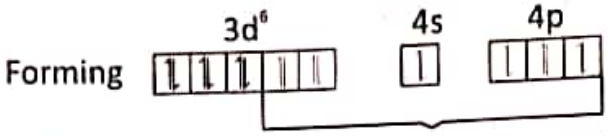
Hence six electrons pairs from 6 N atoms of three ($N_3P_3H_5$) ring has hexadently coordinated to Ni atom forming dimeric complex as -



Ni^{4+} ion accepted 6$\bar{e}$ pairs from 3($P_3N_3H_5$) rings to form $[(P_3N_3H_5)_3 - Ni]_2$ complex and Ni^{2+} has changed into Ni^{3+} in dimer as -

$$Ni^{2+} + Ni^{4+} \rightarrow \underset{\text{(dimer)}}{Ni^{3+}}$$

Form X - ray diffraction pattern of the complex, $Sin^2Ø$ Miller Indices (hkl) and inter planar distance 'd' were calculated. The found values of 'd' concides with theoretical ones (table -2). The values of axial ratio $a_o = b_o = 3.1168$ Å, $c_o = 3.8179$ Å and axial angles $\alpha = \beta = 90°$, $\gamma = 120°$, determined resembles with the hexagonal stereo geometry of the complex which may be expressed by fig-2. The gradation in I/I_o indicate the crystalinity of the complex.

The complex was also tested against the E.coli and Klebsiella (gm-ve), stephylococcus, stephylococci, streptococci, Bacilli (gm+ve) bacteria and Candida albicans fungi to check the effect of this complex on said bacteria and fungi, and it is observed that the complex is active + 13mm against Klebsiella and + 5mm against the Candida albicans fungi, which causes subsequently, urinogenital infection and skin disease in human beings.

Hence the complex may be used as medicine for the both urinogenital and skin infections caused by Klebsiella bactela arid Candida albicans fungi.

ACKNOWLEDGEMENT :

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Table-1 MASS SPECTRUM OF COMPLEX Ni (II). HHCTP

S.No.	m/z Ratio	Fragments
1	120	P_3N_2(M–1)
2	209	$(P_3N_3H_3)$ Ni N (M–2)
3	273	$(P_3N_3H_5)$ – Ni – NP_2 (M–2)
4	460	$(P_3N_3H_5)_2$ – Ni – P_3N_2
5	613	$(P_3N_3H_5)_3$ – Ni – (P_3N_3) (M–1)
6	787	$[(P_3N_3H_5)_2$ – Ni$]_2$ – $(P_2N_3H_4)$ (M–1)
7	815	$[(P_3N_3H_5)_2$– Ni$]_2$ – $(P_3N_3H_5)$ (M–3)
8	923	$[(P_3N_3H_5)_2$– Ni$]_2$ – $(P_3N_3H_5)$ – P_2N_3 (M+1)
9	956	$[(P_3N_3H_5)_3$– Ni – $(P_3N_3H_5)$ – Ni $(P_3N_3H_5)_2$ (M–2) Or $[(P_3N_3H_5)_3$– Ni$]_2$ (M–2)

Table - 2 XRD PATTERN OF COMPLEX $[(N_3P_3H_5)_3$ - Ni$]_2$

S.N.	2θ(°)	$Sin^2\theta$	q $(h^2+k^2+l^2)$	hkl	d(Å) obs. (theo.)	I/I_o
1	21.000	0.0332	0.03320 x (1)	100	4.2277 (4.2267)	100.0
2	26.470	0.0523	0.02615 x (2)	110	3.3666 (3.3656)	006.0
3	30.170	0.0676	0.02254 x (3)	111	2.9615 (2.9606)	025.3
4	34.880	0.0898	0.02245 x (4)	200	2.5702 (2.5700)	037.8
5	42.420	0.1308	0.02616 x (5)	210	2.1296 (2.1290)	045.7
6	48.525	0.1694	0.02823 x (6)	211	1.8714 (1.8710)	032.5
7	55.500	0.2167	0.02708 x (7)	220	1.6544 (1.6543)	006.6
8	57.660	0.2325	0.02583 x (8)	300	1.5974 (1.5973)	009.4
9	66.765	0.3027	0.02751 x (9)	311	1.4002 (1.4000)	005.0

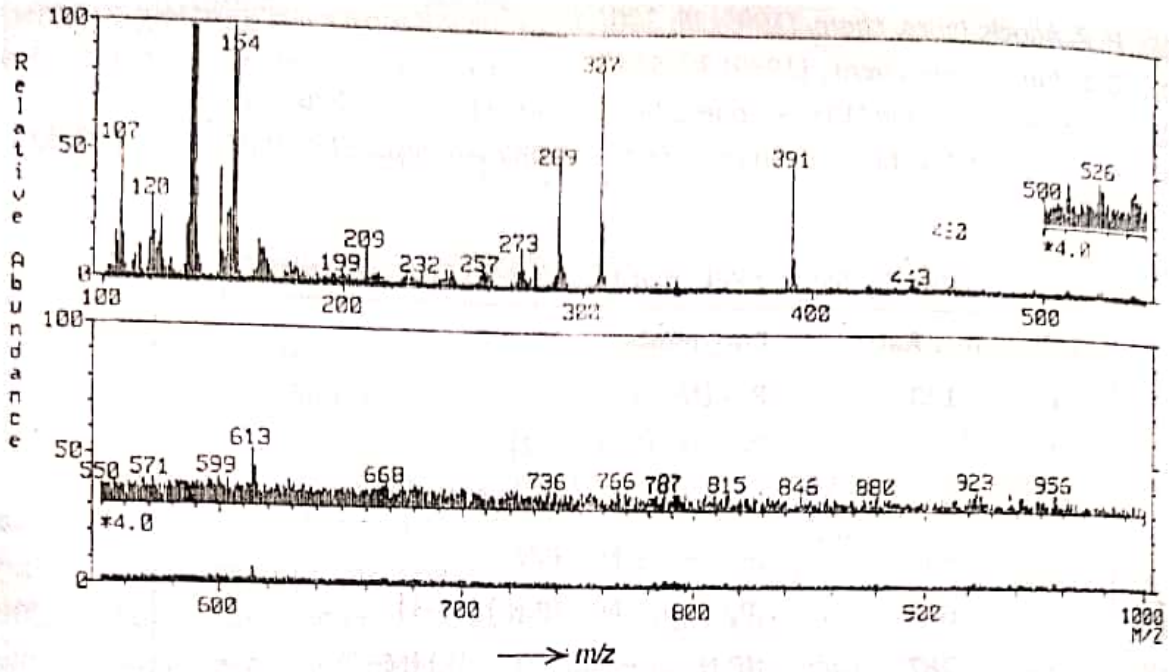

Fig (1) Mass Spectrum of Complex $[(N_3P_3H_5)_3\text{-}Ni]_2$

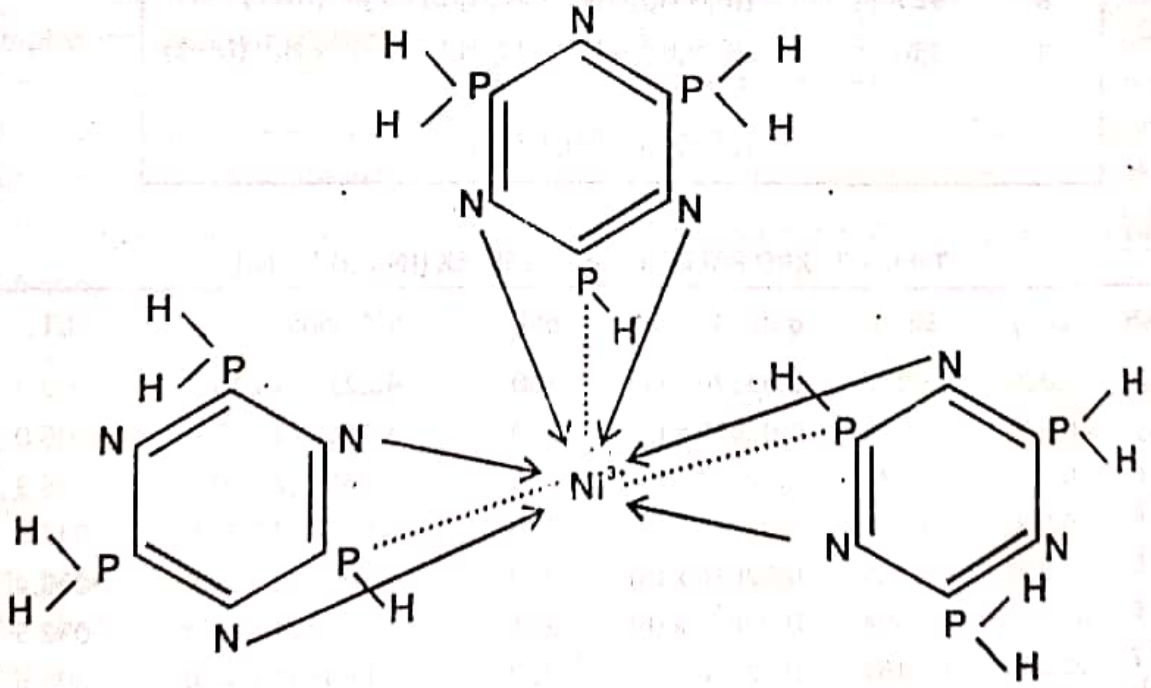

Fig. (2) Proposed Structure of Complex $[(N_3P_3H_5)_3 - Ni]_2$

Effect of Porous Medium on Mhd Viscous Incompressible Fluid Down Between Two Inclined Parallel Flat Plates Under Gravity

GANESH GOPAL VARSHNEY, VIRESH KUMAR VARSHNEY**, AND *N. K. VARSHNEY*.*

ABSTRACT :
In the present paper, the effects of porous medium on MHD unsteady flow of viscous fluid between two inclined parallel flat plates have been studied. The velocity distribution for unsteady flow is obtained . The particular case for steady flow had also been deduced.

Keywords : Porous medium, viscous incompressible fluid, MHD, Parallel flat plate.

INTRODUCTION :

Here we suppose uniform magnetic field applied perpendicular to the flow of viscous fluid down between two inclined parallel flat plates. Snedden (1951) had studied the flow of viscous incompressible fluid down an inclined plate; Sharma et. al. (1995) worked on the steady laminar free convective flow of an electrically conducting fluid along a porous hot vertical plate in the presence of heat source/sink; Ahmed et. al. (1997) discussed on the three dimensional free convective flow and heat transfer through a porous medium; Biswal et. al (2002) have also studied the MHD flow between two infinite parallel plates, one oscillating while other is uniform in motion; Rajeshwara et. al. (2003) studied the unsteady flow through a porous medium in a vertical channel under a transverse magnetic field. Recently Kumar and Singh (2008) studied the magnetic field on the motion under gravity of a viscous fluid down between two inclined parallel flat plates.

In this present paper we extended the research work Kumar and Singh (2008). We investigated the effect of porous medium on velocity distribution for unsteady flow of viscous fluid by using of Fourier Transform. For steady flow of viscous liquid had also deduced.

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FORMULATION AND SOLUTION OF THE PROBLEM :

Consider the motion of a viscous incompressible fluid down in an inclined plate in the presence of magnetic field with the assumption that the velocity of the fluid at the free surface is known and a uniform magnetic field applied perpendicular to the parallel to the flat plates. For the slow motion of viscous liquid governing equations of motion is

$$\frac{\partial v}{\partial t} = -F + \frac{1}{p}\,\text{grad}\,(p) = -\nu\nabla^2 u - \frac{\sigma B_0^2}{p}\,v - \frac{1}{K}\,v \qquad \text{.....(1)}$$

Consider a viscous liquid of density p filling the surface between the two parallel plates with boundaries y = 0, y = h and moving under gravity,

then we may take

$$F = g\,(\sin\alpha - \cos\alpha, 0) \qquad \text{.....(2)}$$

Since motion may be assumed to be the same in all planes parallel to the plane-xy. Vector v will be of the form (u.0.0) where u is the function of x, y and t. Let us suppose that fluid is homogenous.

Equation of continuity is

$$\frac{\partial u}{\partial x} = 0 \qquad \text{.....(3)}$$

$\Rightarrow$ u is the function only of y and t.

Under these circumstance equation (I) becomes

$$\frac{\partial u}{\partial t} = g\sin\alpha - \frac{1}{p}\frac{\partial p}{\partial x} + \nu\frac{\partial^2 u}{\partial y^2} - \frac{\sigma B_0^2}{\rho}\,u - \frac{1}{K}\,u \qquad \text{.....(4)}$$

$$0 = g\cos\alpha - \frac{1}{\rho}\frac{\partial p}{\partial y} \qquad \text{.....(5)}$$

Clearly $\left\{ g\sin\alpha \; \frac{1}{\rho}\frac{\partial p}{\partial y} \right\}$ is a function of y alone, and hence from equation

(5), We have

$$p = \rho g (x \sin\alpha - y \cos\alpha) + x\rho X \qquad \ldots\ldots (6)$$

Where X is Constant

Therefore equation (4) becomes

$$\frac{\partial u}{\partial t} = -X + \nu \frac{\partial^2 u}{\partial y^2} - \frac{\sigma B_0^2}{\rho} u - \frac{1}{K} u \qquad \ldots\ldots (7)$$

Now introduce the Finite Fourier Sine Transform

$$Us(n,t) = \int_0^h u(y,t) \sin\left(\frac{n\pi y}{h}\right) dy \qquad \ldots\ldots (8)$$

Subject to the boundary conditions :

$u = U(t)$, on $y = h$

$u = 0$ on $y = 0$

i.e. $u(0,t) = 0$ at $y = 0$

and $u(h,t) = 0$ at $y = h$ $\qquad \ldots\ldots (9)$

Multiply (7) by $\sin\left(\frac{n\pi y}{h}\right)$ and integrating with respect to y,

from $0 \to h$, and using equation (9) we get

$$\int_0^h \frac{\partial u}{\partial t} \sin\frac{n\pi y}{h} dy = X + \nu \int_0^h \frac{\partial^2 u}{\partial y^2} \sin\frac{n\pi y}{h} dy - \left(\frac{\sigma B_0^2}{\rho} + \frac{1}{K}\right) \int_0^h u \sin\frac{n\pi y}{h} dy$$

$$\text{or } \frac{du_s}{dt} + \left(\nu \frac{n^2\pi^2}{h^2} + \frac{\sigma B_0^2}{\rho} + \frac{1}{K}\right) u_s = -X + (-1)^{n+1} \nu \frac{n\pi}{h} U(t) \qquad \ldots\ldots (10)$$

This is ordinary linear equation. Solving equation (10), we get

$$u_s = -X\frac{1}{\left(v\frac{n^2\pi^2}{h^2}+\frac{\sigma B_0^2}{\rho}+\frac{1}{K}\right)}+(-1)^{n+1}v\frac{n\pi}{h}\int_{t_0}^{t}U(t)e^{\left(\frac{vn^2\pi^2}{h^2}+\frac{\sigma B_0^2}{\rho}+\frac{1}{K}\right)(t-\tau)}$$

..... (11)

Where t_0 is an arbitrary time defined by the initial conditions.

Using inverse formula for Finite Fourier Sine form, we g

$$u(y,t)=\frac{2}{h}\sum_{n=1}^{\infty}\left[-X\frac{1}{\left(v\frac{n^2\pi^2}{h^2}+\frac{\sigma B_0^2}{\rho}+\frac{1}{K}\right)}+(-1)^{n+1}v\frac{n\pi}{h}\int_{t_0}^{t}U(t)e^{-\left(\frac{vn^2\pi^2}{h^2}+\frac{\sigma B_0^2}{\rho}+\frac{1}{K}\right)(t-\tau)}d\tau\right]$$

$$x\sin\frac{n\pi y}{h}$$

..... (12)

If flow is steady, then U (t) is constant, therefore equation (9) becomes

$$\left(v\frac{n^2\pi^2}{h^2}+\frac{\sigma B_0^2}{\rho}+\frac{1}{K}\right)u_s=-X+(-1)^{n+1}v\frac{n\pi}{h}U$$

$$\text{or}\quad u_s=-X\frac{1}{\left(v\frac{n^2\pi^2}{h^2}+\frac{\sigma B_0^2}{\rho}+\frac{1}{K}\right)}+(-1)^{n+1}\frac{vn\pi U}{\left(v\frac{n^2\pi^2}{h^2}+\frac{\sigma B_0^2}{\rho}+\frac{1}{K}\right)}$$

..... (13)

Now using inverse formula for the Finite Fourier Sine Transform, we get

$$u(y,t)=\frac{2}{h}\sum_{n=1}^{\infty}\left[-X\frac{1}{\left(v\frac{n^2\pi^2}{h^2}+\frac{\sigma B_0^2}{\rho}+\frac{1}{K}\right)}+(-1)^{n+1}\frac{vn\pi U}{\left(v\frac{n^2\pi^2}{h^2}+\frac{\sigma B_0^2}{\rho}+\frac{1}{K}\right)}\right]\sin\frac{n\pi y}{h}$$

DISCUSSION :

The expression for velocity distribution of unsteady flow is given by equation (12) and the velocity distribution for steady flow is given by equation (14) respectively.

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High-Temperature Elastic Constants for Ionic Materials Using Equation of State

S. P. Singh*

ABSTRACT :

In this paper, a new expression for temperature dependence of elastic constants are developed using equation of state for the temperature dependence of bulk modulus and the formulation derived from Tallon's method based on thermodynamic analysis. The proposed equation of state is applied to investigate the study high temperature elastic constants for ionic materials. The computed values of second order elastic constants at high temperature have shown a good agreement with available experimental results. It is concluded that a new expression for SOE constants is capable to predict the elastic properties for minerals as well as minerals relevant to geophysics under high temperature conditions.

Key Words : EOS; SOEC; Ionic Materials; High temperature

INTRODUCTION :

The study of elastic properties of minerals is essential for examining and understanding of the dynamics of earth's deep interior, structure and composition of earth's lower mantle and in seismic studies [1]. The elasticity offers more information than the volume in interpreting the temperature dependence of equation of state (EOS) because the compressibility is defined by the derivative of volume. Thermal expansivity is a very important parametric quantity for interpreting the thermodynamic and thermo elastic behaviour of minerals at high temperatures because it has been emphasized [2] that most of the serious errors in the calculations of thermodynamic functions arise due to uncertainty of thermal expansivity at high temperatures. The behaviors of elastic properties under the effect of high pressure and high temperature have attracted the attention of experimental [3-5] as well as theoretical workers [6-9].

In the present study, a new relation for temperature dependence of elastic constants are developed using equation of state for the temperature dependence of bulk modulus and the formulation derived from Tallon's method based on thermodynamic

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Where δ°_{T} is the value of Anderson-Gruneisen parameter at $T = T_0$, and $X = T/T_0$, T_0 is the reference temperature, k is the new dimension less parameter which can be calculated from the slope of the graph plotted between log δ°_{T} and log(T/T_0). If we thus substitute the value of δ_T from Eq. (8) in Eq. (5), we can be obtained the modified expression for thermal expansion coefficient as follows:

$$\delta^{\circ}_{T} X^{k} = \frac{1}{\alpha^{2}} \left(\frac{\partial \alpha}{\partial T}\right)_{P} \qquad \text{---------- (9)}$$

or $$\delta^{\circ}_{T} \left(\frac{T}{T_0}\right)^{k} = \frac{1}{\alpha^{2}} \left(\frac{\partial \alpha}{\partial T}\right)_{P} \qquad \text{---------- (10)}$$

By integrating Eq. (10), we have

$$\frac{\delta^{\circ}_{T}}{T_0^{k}} \frac{T_0^{k+1}}{(k+1)} = -\frac{1}{\alpha_T} + C \qquad \text{---------- (11)}$$

Where C is an integration constant evaluated from initial conditions at $T = T_0$ and $\alpha_T = \alpha_0$,

$$\frac{\delta^{\circ}_{T}}{T_0^{k}\,(k+1)} \left(T^{k+1} - T_0^{k+1}\right) = \frac{1}{\alpha_0} - \frac{1}{\alpha_T} \qquad \text{---------- (12)}$$

The final expression for thermal expansivity is thus obtained as

$$\frac{\alpha_T}{\alpha_0} = \left[1 - \frac{\alpha_0 \delta^{\circ}_{T}}{T_0^{k}\,(k+1)} \left(T^{k+1} - T_0^{k+1}\right)\right]^{-1} \qquad \text{---------- (13)}$$

If the empirical temperature dependence of δ_T is assumed then Eq.(4) at P = 0, may also written as follows:

$$-\left(\frac{\partial K_T}{\partial T}\right)_{P} = \alpha_0 K_0 \delta_T \qquad \text{---------- (14)}$$

Using Eq.(8), we have

$$\delta^{\circ}_{T} \left(\frac{T}{T_0}\right)^{k} = -\frac{1}{\alpha_0 K_0} \left(\frac{\partial K_T}{\partial T}\right)_{P} \qquad \text{---------- (15)}$$

Integrating Eq. (15), we have

$$\int_{K_0}^{K_T} dK_T = -\alpha_0 K_0 \delta^{0}_{T} \int_{T_0}^{T} \left(\frac{T}{T_0}\right)^{k} dT \qquad \text{---------- (16)}$$

Thus, we get the final expression for the bulk modulus K_T is

$$K_T = K_0 \left[1 - \frac{\alpha_0 \delta^{\circ}_{T}}{T_0^{k}\,(k+1)} \left(T^{k+1} - T_0^{k+1}\right)\right] \qquad \text{---------- (17)}$$

5, respectively. In both equations (17) and (22) needs only three input parameters such as Anderson Grunesian parameter (δ_T°), volume thermal expansion coefficient (α_0) at zero pressure and the thermo-elastic parameter K which can be calculated from the graph between log (δ_T°) and log (T/T_0). The values of parameter *k* are shown in Table-1 for ionic materials. The values of bulk modulus (K_T) calculated at different temperatures using equation (17) are reported in Tables 2-5 along with the experimental data [1.3] for comparison. In all cases, it has been found that the equation (17) improves the results as compared with other theoretical studies [8, 17-20]. The maximum deviations are found at highest temperatures. We have therefore calculated the percentage deviations at highest temperatures and reported in Table 6. In all cases, the deviations are less. A good agreement obtained for the temperature dependence of bulk modulus, encouraged the authors to extend these theory for the study of the temperature dependence of second order elastic constants. Equation (17) may be generalized in the form of Eq. (21). Equation (21) may be written for the second-order elastic constants (SOEC) in the form of Eq. (22) which is used to compute the temperature dependence of SOEC of MgO, CaO, NaCl, and KC1. Thus the results obtained are listed in Tables 2-5 for the second order elastic constants for these four ionic materials under study present reasonably good agreement with the available experimental data [3] expect in few cases. The percentage deviations calculated at highest temperatures are reported in Table 6. In general, the deviations are in C_{12}. The abnormal behavior of the temperature dependence of elastic constant C_{12} is related to the existence of many body potential and non-central potentials in solids, which are responsible for the break down of the Cauchy relation = C_{44}. The variation of C_{11} with temperature is found to be larger as compared with C_{12} and C_{44}. The constant C_{11} represent elasticity in length. A longitudinal strain produces a change in volume without a change in shape. The volume change is highly related to the temperature and thus produces a large change in C_{11}. On the other hand, the constants C_{12} and C_{44} are related to the elasticity in shape which is shear constant. A transverse strain of shearing causes a change in shape without a change in volume. Thus C_{12} and C_{44} are less sensitive of temperature as compared with C_{11}.

We have thus presented a simple and straightforward method, to study the elastic properties of ionic materials under varying conditions of temperature. The results obtained are demonstrated and encouraging that the present method is far better as compared with earlier studies [8, 17-20]. Due to the simplicity of the method, it can be extended to more complex solids like minerals of geophysical importance and applications.

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Table 1 : Values of input parameters [1, 3]. k (dimensionless), αo in ($10^{-5}K^{-1}$) and δ_n (dimensionless).

Parameters	MgO	CaO	NaCl	KCl
k	-0.019	-0.024	-0.025	-0.012
αo	3.12	3.04	11.8	11.0
δo	5.3	6.19	5.2	5.84
δ011	6.27	7.31	6.28	7.48
δ0012	-2.49	-2.0	0.051	-3.31
δ044	2.57	2.88	2.35	3.04

Table 2 : Calculated values of C_{11}, C_{12}, C_{44} and K_T (in Gpa) for MgO at different temperatures T (in K) using Eq. (22, 17) along with the experimental data [1, 3].

T	C_{11}		C_{12}		C_{44}		K_T	
	Eq.(22)	Exp. [3]	Eq.(22)	Exp. [3]	Eq.(22)	Exp. [3]	Eq.(17)	Exp. [1]
300	298.96	298.96	96.42	96.42	157.13	157.13	161.6	161.6
400	293.09	292.94	97.17	97.14	155.87	155.78	158.95	158.9
500	287.21		97.92		154.59		156.32	156.1
600	281.31	280.62	98.68	98	153.33	152.84	153.7	153.2
700	275.4		99.44		152.05		151.08	150.4
800	269.49	268.22	100.19	98.54	150.78	149.68	148.48	147.4
900	263.56		100.95		149.5		145.88	144.3
1000	257.64	255.74	101.71	98.74	148.22	146.52	143.28	141.4
1100	251.71		102.47		146.95		140.69	138.3
1200	245.78	243.22	103.23	98.38	145.67	143.06	138.11	135.1
1300	239.84		103.99		144.39		135.53	132.1
1400	233.91	230.96	104.75	97.56	143.12	139.54	132.95	128.1
1500	227.97		105.51		141.83		130.38	125.7
1600	222.03	219.04	106.27	96.44	140.55	136.24	127.8	122.5
1700	216.09		107.03		139.27		125.24	119.6
1800	210.15	208	107.79	95.02	137.99	133.12	122.67	116.6

Table 3 : Calculated values of C_{11}, C_{12}, C_{44} and K_T (in Gpa) for CaO at different temperatures T (in K) using Eq. (22. 17) along with the experimental data [1, 3].

T	C_{11}		C_{12}		C_{44}		K_T	
	Eq.(22)	Exp. [3]	Eq.(22)	Exp. [3]	Eq.(22)	Exp. [3]	Eq.(17)	Exp. [1]
300	220.5	220.5	57.67	57.67	80.03	80.03	111	111
400	215.59	215.7	58.02	57.96	79.32	79.35	108.94	109
500	210.65	210.7	58.37	58.23	78.61	78.7	106.91	106
600	205.71	205.9	58.72	58.44	77.89	77.94	104.88	104
700	200.75	201.2	59.08	58.66	77.18	77.18	102.86	102
800	195.78	196.6	59.44	58.81	76.46	76.46	100.84	100
900	190.81	192	59.79	58.98	75.75	75.72	98.83	98
1000	185.84	187.2	60.15	58.98	75.03	74.92	96.83	96
1100	180.86	182.7	60.5	58.96	74.31	74.17	94.84	94
1200	175.88	178.1	60.86	58.99	73.59	73.48	92.84	92

Table 4 : Calculated values of C_{11}, C_{12}, C_{44} and K_T (in Gpa) for NaCl at different temperatures T (in K) using Eq. (22, 17) along with the experimental data [1,3].

T	C_{11}		C_{12}		C_{44}		K_T	
	Eq.(22)	Exp. [3]	Eq.(22)	Exp. [3]	Eq.(22)	Exp. [3]	Eq.(17)	Exp. [1]
300	49.5	49.5	13.2	13.2	12.79	12.79	24	24
350	47.67	47.6	13.19	13.3	12.61	12.62	23.26	23.2
400	45.85	45.8	13.19	13.4	12.43	12.43	22.52	22.4
450	44.03	44.1	13.18	13.5	12.26	12.26	21.77	21.6
500	42.21	42.4	13.18	13.6	12.08	12.09	21.03	20.8
550	40.4	40.5	13.18	13.5	11.91	11.09	20.28	19.9
600	38.59	38.7	13.17	13.2	11.73	11.71	19.53	19
650	36.78	37	13.17	13.1	11.56	11.52	18.78	18.1
700	34.98	35.4	13.16	13.1	11.39	11.31	18.03	17.3
750	33.17	33.7	13.16	12.9	11.21	11.1	17.28	16.5

Table 5 : Calculated values of C_{11}, C_{12}, C_{44} and K_T (in Gpa) for KC1 at different temperatures T (in K) using Eq. (22, 17) along with the experimental data [1,3].

T	C_{11}		C_{12}		C_{44}		K_T	
	Eq.(22)	Exp. [3]	Eq.(22)	Exp. [3]	Eq.(22)	Exp. [3]	Eq.(17)	Exp. [1]
300	40.1	40.1	6.6	6.6	6.35	6.35	17	17
350	38.45	38.4	6.72	6.8	6.24	6.28	16.45	16.4
400	36.79	36.9	6.84	7	6.14	6.21	15.91	15.9
450	35.14	35.4	6.96	7.1	6.03	6.15	15.36	15.4
500	33.48	33.8	7.08	7.2	5.92	6.11	14.82	14.7
550	31.82	32.3	7.2	7.3	5.81	6.05	14.28	14.2
600	30.16	31.1	7.32	7.5	5.7	5.96	13.74	13.7
650	28.5	29.7	7.44	7.7	5.6	5.87	13.2	13.2
700	26.84	28.2	7.56	7.7	5.49	5.79	12.65	12.6
750	25.18	26.6	7.68	7.7	5.38	5.69	12.11	12
800	23.52	25.2	7.81	7.8	5.28	5.57	11.57	11.5
850	21.85	23.5	7.93	7.7	5.17	5.57	11	10.9

Table 6 : Percentage deviations at highest temperatures using present theory for which the experimental data are available.

MgO	C_{11}	C_{12}	C_{44}	B_T	NaCl	C_{11}	C_{12}	C_{44}	K_T
T = 1800 K	1.03	13.43	3.65	5.2	T = 750 K	1.57	2.01	0.99	4.72
CaO	C_{11}	C_{12}	C_{44}	B_T	KCl	C_{11}	C_{12}	C_{44}	K_T
T = 1200 K	1.24	3.17	0.15	0.91	T = 850 K	7.02	2.98	7.18	0.91

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