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ORIGINAL ARTICLE

Thermodynamic properties of binary mixtures of 1,3,4-oxadiazole derivative with chloroform, *N*,*N*-dimethyl formamide at 303, 308 and 313 K and atmospheric pressure

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Abstract The density (ρ), viscosity (η) and ultrasonic velocity (U) of pure solvents (chloroform (CF), *N*,*N*-dimethyl formamide (DMF)) and solutions of 2-((4-acetyl-5-(2-hydroxyphenyl)-5-methyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-*o*-tolylquinazolin-4(3*H*)-one (PD_{I-C}) (0.001, 0.002, 0.004, 0.006, 0.008, and 0.010 mol dm^{-3}) in CF and DMF are investigated at 303, 308 and 313 K at atmospheric pressure. Various thermodynamic parameters such as acoustical impedance (Z), adiabatic compressibility (κ_a), inter molecular free path length (L_f), Rao's molar sound function (R_m), Van der Waals constant (b), internal pressure (π), relaxation time (τ), free volume (V_f) and solvation number (S_n) are calculated by using ρ, η and U data. The results obtained are interpreted in terms of solute–solvent and solute–solute interactions. The structure making or structure-breaking abilities of the solute in CF and DMF solvent are also studied.

1. Introduction

The five member 1,3,4-oxadiazole heterocycles are useful intermediates for the development of molecules of pharmaceutical interest where several promising antitumor compounds are found to contain the oxadiazole ring system (Rostom et al., 2003; Kumar et al., 2009). 1,3,4-Oxadiazole heterocycles are good bioisosteres of amides and esters, which can contribute substantially in increasing pharmacological activity by participating in hydrogen bonding interactions with the receptors (Guimaraes et al., 2005). The 2,5-disubstituted-1,3,4-oxadiazole derivatives are known for various pharmacological activities such as antibacterial (El-Emam et al., 2004), anti-inflammatory (Mullican et al., 1993), analgesic (Khan and Akhtar, 2003), antiviral and anticancer (Shah et al., 1998), antihypertensive (Upadhyay and Ram, 1999), anticonvulsant (Khan et al., 2001), antiproliferative (Liszkiewicz et al., 2003; Zahid et al., 2009), herbicidal (Kennedy and summers, 1981),

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Nomenclature

C (mol dm^{-3})	concentration
T (K)	absolute temperature
M (kg mol^{-1})	molecular weight of solutions
M_1	molecular weight of solvent
M_2	molecular weight of solute
W_1	weight fraction of solvent
W_2	weight fraction of solute
R (J mol^{-1} K^{-1})	universal gas constant
b (m^3)	Van der Waals constant
m	meter
Pa	pascle
s	second
κ_b	Boltzmann constant
h	Plank's constant

Greek symbol

ρ (kg m^{-3})	density
η (mPa s)	viscosity
U (m s^{-1})	ultrasonic velocity
Z (kg m^{-2} s^{-1})	specific acoustical impedance
$_a$ (Pa–1)	adiabatic compressibility
L_f (m)	intermolecular free length
R_m (m10/3 s^{-1}/3 mol^{-1})	Rao's molar sound function
π (Pa)	internal pressure
V_f (m^3)	free volume

Superscripts

CF	chloroform
DMF	*N,N*-dimethyl formamide
A R	analytical reagent

hypoglycemic (O'Neal et al., 1962), hypnotic and sedative (Adelstein et al., 1976), MAO inhibitor (Mazouz et al., 1990) and insecticidal (Misra, 1983).

The sound velocity is a purely thermodynamic property. Many thermodynamic properties can be elucidated from sound velocity, viscosity and density data. Thermodynamic data are very important tool for understanding molecular interaction; solute–solvent and solute–solute, occurring in the solution. In recent years, the measurements of ultrasonic velocity have been adequately employed in understanding the nature of molecular interaction in pure liquids, binary and ternary mixtures (Srinivasalu and Ramachandra Naidu, 1991; Varadarajalu and Lakshminarayanan Reddy, 1998; Aswar, 1998). A literature survey reveals that ultrasonic velocity of various organic, inorganic and biological compounds in various solvents has been studied (Zhang et al., 2011; Baluja and Oza, 2002; Baluja and Shah, 2004). Our research group has also studied acoustical properties of synthesized compounds in various solvents (Godhani and Parsania, 2002; Godhani et al., 2001).

The choice of 1,3,4-oxadiazole is due to its multi-applicability in the field of medicine. The applications of these compounds attract us to study their behavior in various solvents and also investigate their thermodynamic properties. In the present paper, we have used this technique for the better understanding of the molecular interactions in some solutions. The present work deals with thermodynamic properties of the newly synthesized 1,3,4-oxadiazole derivative of 2-((4-acetyl-5-(2-hydroxyphenyl)-5-methyl-4,5-dihydro-1,3,4-oxadiazol-2-yl) methylthio)-3-*o*-tolylquinazolin-4(3*H*)-one ($PD_{I–C}$) in chloroform (CF) and *N,N*-dimethyl formamide (DMF) solutions at 303, 308 and 313 K and at atmospheric pressure. The results are interpreted in terms of molecular interaction occurring in the solutions.

2. Experimental

2.1. Materials

The 2-((4-acetyl-5-(2-hydroxyphenyl)-5-methyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-*o*-tolylquinazolin-4(3*H*)-one ($PD_{I–C}$) used in this study was synthesized in our laboratory. The molecular weight of $PD_{I–C}$ is 500.15. The structure of $PD_{I–C}$ was confirmed by IR, ^1H NMR and CHN analyses. The structure of the present synthesized new $PD_{I–C}$ is shown in Fig. 1. The solvents: chloroform (CF) and *N,N*-dimethyl formamide (DMF) used in the present study were of A R grade and were purified according to literature methods (Riddick et al., 1986). The estimated purity of solvents was more than 99.8% and was confirmed by HPLC with PDA detector. The schiff-base of (*Z*)-*N*′-(2-hydroxybenzylidene)-2-(4-oxo-3-*o*-tolyl-3,4-dihydroquinazolin-2-ylthio)acetohydrazide was synthesized in our laboratory (Sanghani et al., 2008). The 1,3,4-oxadiazole derivative of 2-((4-acetyl-5-(2-hydroxyphenyl)-5-methyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-*o*-tolylquinazolin-4(3*H*)-one ($PD_{I–C}$) was synthesized by reacting schiff-base with acetic anhydride and was purified three times from chloroform – *n*-hexane prior to its use.

2.2. Synthesis of 2-((4-acetyl-5-(2-hydroxyphenyl)-5-methyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-o-tolylquinazolin-4(3H)-one ($PD_{I–C}$)

A mixture of Schiff-base 0.005 mol (2.50 g) and acetic anhydride (10 mL) was taken into a 100 mL round bottomed flask

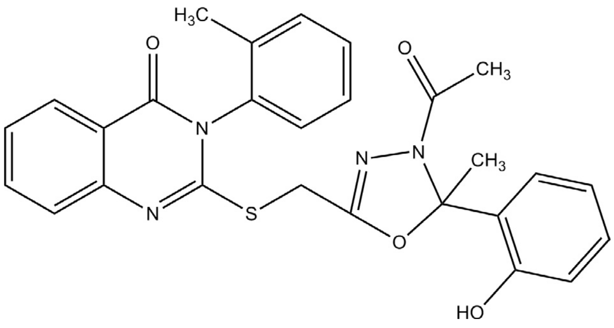

Figure 1 Structure of 2-((4-acetyl-5-(2-hydroxyphenyl)-5-methyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-*o*-tolylquinazolin-4(3*H*)-one ($PD_{I–C}$).

and was refluxed for 3.5 h in an oil bath. The progress of the reaction was monitored with the aid of TLC. The excess of acetic anhydride was then distilled off and the remaining mixture was poured in the ice cold water to form a yellowish solid compound $PD_{I\text{–}C}$. The product was separated by filtration and crystallized from chloroform – *n*-hexane to afford the title compound $PD_{I\text{–}C}$. The purity of the compound was checked by aluminum coated TLC plates 60 F_{245} (E. Merck) and the compound is purified by column chromatography using silica gel (60–120 mesh) and chloroform: *n*-hexane as an eluent. Yield – 63%, m.p. 248 °C.

Anal. calc. for $C_{27}H_{24}N_4O_3S$: C–64.78; H–4.83; N–11.19%. Found: C–64.75; H–4.85; N–11.22%.

FT–IR: 3070 cm^{-1} (Ar–H), 2933 cm^{-1} (C–H asym. str.), 2851 cm^{-1} (C–H sym. str.), 1708 cm^{-1} (CdbndN str.), 1520 cm^{-1} (CdbndC str.), 1475 cm^{-1} (–CH_2 ben.), 1386 cm^{-1} (–CH_3 ben.), 1273 cm^{-1} (C–N str.), 1012 cm^{-1} (C–O abs.), 755 cm^{-1} (1,2–disubstituted ring).

^{1}H NMR: 8.39–8.41 δppm (1H, d), 7.70–7.78 δppm (4H, m), 7.73–7.75 δppm (1H, d), 6.90–7.20 δppm (6H, m), 4.93 (1H, s), 2.52 δppm (2H, s), 2.66 δppm (6H, s), 1.85 δppm (3H, s).

2.3. *Measurements of density, viscosity and ultrasonic velocity*

2.3.1. *Apparatus and procedure*

All the samples were prepared freshly and retained at the desired temperature for 24 h to ensure their solubility at the temperature. Samples were kept in bottles with PTFE septum under vacuum until further use.

2.3.2. *Density, viscosity and ultrasonic velocity*

Ultrasonic velocity, density and viscosity measurements in pure solvents (CF and DMF) and solutions of compound $PD_{I\text{–}C}$ (0.001, 0.002, 0.004, 0.006, 0.008, and 0.010 mol dm^{-3}) in CF and DMF were made at 303, 308, and 313 K, by using M–81 multi frequency ultrasonic interferometer (2 MHz) (Mittal Enterprise, New Delhi), a Single Capillary Pycnometer made of borosil glass having a bulb capacity of 10 mL and an Ubbelohde viscometer. The Ubbelohde viscometer with 25 mL capacity was used for the viscosity measurement. Ubbelohde viscometer was calibrated with fresh conductivity water immersed in a water bath that was maintained at the experimental temperature. The flow time of water (t_w) and the flow time of solution (t_s) were measured with a digital stop clock with an accuracy of ±0.01 s (Model: RACER HS–10 W). Ultrasonic velocity (U), density (ρ) and viscosity (η) measurements were accurate to ±0.1 m s^{-1}, ±0.1 kg m^{-3} and ±0.003 mPa s, respectively. The uncertainty of temperature is ±0.01 K and that of solution concentrations is ±0.0001 mol dm^{-3}. The values of Ultrasonic velocity (U), density (ρ) and viscosity (η) were average of at least three measurements and the reproducibility of measurement values for sample.

2.3.2.1. *Theoretical equations.* From the experimental data of density, viscosity and ultrasonic velocity, various acoustical parameters are evaluated using standard equations:

Adiabatic compressibility:

$$\kappa_a = 1/U^2\rho \tag{1}$$

Rao's molar sound function (Bagchi et al., 1986):

$$R_m = (M/\rho)U^{1/3} \tag{2}$$

where M is the apparent molecular weight of solution and can be calculated according to the following equation: $M = M_1W_1 + M_2W_2$where W_1 and W_2 are weight fractions of solvent and solute respectively. M_1 and M_2 are molecular weights of the solvent and solute respectively.

Van der Waals constant (Vigoureux, 1952):

$$b = M/\rho\{1 - [RT/(MU^2)][\sqrt{(}1 + (MU^2)/3RT) - 1]\} \tag{3}$$

where R {8.3143 (J K^{-1} mol^{-1})} is the gas constant and {T (K)} is absolute temperature.

Internal pressure (Suryanarayana, 1979):

$$\pi = b'RT(K\eta/U)^{1/2}(\rho^{2/3}/M^{7/6}) \tag{4}$$

Table 1 Comparison of measured density (ρ), viscosity (η) and ultrasonic velocity (U) data for pure CF and DMF with literature values at 303, 308 and 313 K.

Organic liquids	Present work			Literature		
	T = 303 K	T = 308 K	T = 313 K	T = 303 K	T = 308 K	T = 313 K
	ρ (kg m^{-3})			ρ (kg m^{-3})		
CF	1475.3	1470.8	1465.8	1475.4[a]	1472.7[a]	1467.6[a]
DMF	941.7	937.2	933.6	939.7[b]	936.8[e]	929.8[h]
	η (mPa s)			η (mPa s)		
CF	0.6628	0.6279	0.5781	0.6080[d]	0.6393[f]	0.5460[d]
DMF	0.7588	0.7056	0.6353	0.7520[c]	0.7070[c]	0.6641[c]
	U (m s^{-1})			U (m s^{-1})		
CF	960.0	950.8	932.4	959.0[d]	949.6[a]	933.6[a]
DMF	1442.0	1432.0	1402.0	1446[g]	1426[g]	1404[g]

[a] (Bhuva and Parsania, 2011).
[b] (Pal and Singh, 1995).
[c] (Joshi et al., 1990).
[d] (Amrutia et al., 2006).
[e] (Baluja et al., 2004).
[f] (Kulshrestha and Baluja, 2010).
[g] (Regmi, 2007).
[h] (Chen et al. 1995).

Table 2 The density (ρ), viscosity (η) and ultrasonic velocity (U) of PD_{I-C} in CF and DMF solutions at 303, 308 and 313 K.

Concentration of PD_{I-C} solutions (mol dm^{-3})	Chloroform + PD_{I-C} system			DMF + PD_{I-C} system		
	ρ (kg m^{-3})	η (mPa s)	U (m s^{-1})	ρ (kg m^{-3})	η (mPa s)	U (m s^{-1})
	T = 303 K			T = 303 K		
0.000	1475.3	0.6628	960.0	941.7	0.7588	1442.0
0.001	1476.7	0.6642	968.0	943.2	0.7608	1447.2
0.002	1476.8	0.6650	971.2	943.3	0.7623	1448.4
0.004	1476.9	0.6665	972.8	943.4	0.7641	1450.4
0.006	1477.2	0.6678	974.4	943.6	0.7672	1452.4
0.008	1477.8	0.6696	976.0	943.8	0.7695	1453.6
0.010	1478.1	0.6705	980.8	944.4	0.7724	1456.8
	T = 308 K			T = 308 K		
0.000	1470.8	0.6279	950.8	937.2	0.7056	1432.0
0.001	1471.1	0.6295	958.0	939.3	0.7086	1434.8
0.002	1471.3	0.6303	960.0	939.6	0.7102	1435.6
0.004	1471.6	0.6315	964.0	940.3	0.7128	1436.8
0.006	1471.9	0.6328	965.2	940.8	0.7137	1438.4
0.008	1472.4	0.6341	967.2	941.4	0.7176	1440.4
0.010	1472.9	0.6358	970.0	942.2	0.7213	1443.2
	T = 313 K			T = 313 K		
0.000	1465.8	0.5781	932.4	933.6	0.6353	1402.0
0.001	1465.9	0.5798	941.2	936.1	0.6383	1407.6
0.002	1466.2	0.5806	942.4	936.5	0.6401	1410.4
0.004	1466.6	0.5818	943.2	937.0	0.6415	1414.4
0.006	1467.2	0.5834	944.8	937.3	0.6439	1416.0
0.008	1468.1	0.5848	946.4	938.0	0.6463	1420.4
0.010	1468.8	0.5868	948.0	938.7	0.6501	1426.0

where R {8.3143 (J K^{-1} mol^{-1})} is the gas constant and b' (2) is the packing factor and K (4.28×10^9) is a constant.

Solvation number:

$$S_n = M_2/M_1[(1 - k_a)/k_{a1}][(100 - X)/X] \quad (5)$$

where X is the number of grams of solute in 100 g of the solution. M_1 and M_2 are the molecular weights and κ_{a1} and κ_a are adiabatic compressibility of solvent and solute respectively.

Free volume (Surayanarayana and Kuppusami, 1976):

$$V_f = [MU/K\eta]^{3/2} \quad (6)$$

Intermolecular free path length (Jacobson et al., 1954):

$$L_f = \kappa_j \kappa_a^{1/2} \quad (7)$$

where κ_j {$(93.875 + 0.375T) \times 10^{-8}$} is a temperature-dependent Jacobson's constant.

3. Results and discussion

The density (ρ), viscosity (η) and ultrasonic velocity (U) of pure solvents chloroform (CF) and *N,N*-dimethylformamide (DMF) used in the present work are reported in Table 1 and compared with the available literature data and a satisfactory agreement was found. The ρ, η and U of pure solvents and solutions of 2-((4-acetyl-5-(2-hydroxyphenyl)-5-methyl-4,5-dihydro-1,3,4-oxadiazol-2-yl)methylthio)-3-*o*-tolylquinazolin-4(3*H*)-one (PD_{I-C}) in CF and DMF were measured at 303, 308 and 313 K and are reported in Table 2. It is clear from Figs. 2–4 that ρ, η and U increased with concentration (C) and decreased with temperature (T). The concentration and temperature dependence of these data were tested by least square analysis. Least square means that the overall solution minimizes the sum of the squares of the errors made in solving every single equation. The degree of linearity was judged on the basis of correlation coefficient. A fairly good to excellent correlation between the given parameters and concentration was observed at three temperatures in different solvent systems. The observed correlation between ρ and C, η and C, and U and C is R^2 = 0.900–0.996, 0.972–0.996 and 0.945–0.991 respectively. The obtained R^2 values supported a fairly good to excellent linear dependence of ρ, η and U with C and T. The observed trends for different C and T in ρ, η and U were CF > DMF, DMF > CF and DMF > CF respectively (Figs. 2–4). The increased ρ, η and U with C suggest that the increase of cohesive forces is due to powerful molecular interactions, while the decrease of these parameters with T indicates that cohesive forces decreased. The increasing temperature has two opposite effects namely increase of molecular interaction (structure formation) and destruction of structure formed previously. When the thermal energy is greater than the interaction energy, it causes the destruction of previously formed structure. Thus, the increase of T favors the increase of kinetic energy and volume expansion and hence, results in the decrease of ρ and η.

The density and viscosity of medium, pressure, temperature etc. affect the velocity. With a view to understand the effect of concentration, temperature, nature of solvents and the structure of PD_{I-C} on structure forming or structure-breaking tendency various acoustical parameters like acoustical impendence (Z), adiabatic compressibility (κ_a), intermolecular free path length (L_f), Rao's molar sound function (R_m), Van der Waals constant (b), internal pressure (π), free volume (V_f) and solvation number (S_n) were determined by using the experimental data of ρ, η and U of PD_{I-C} solutions in CF

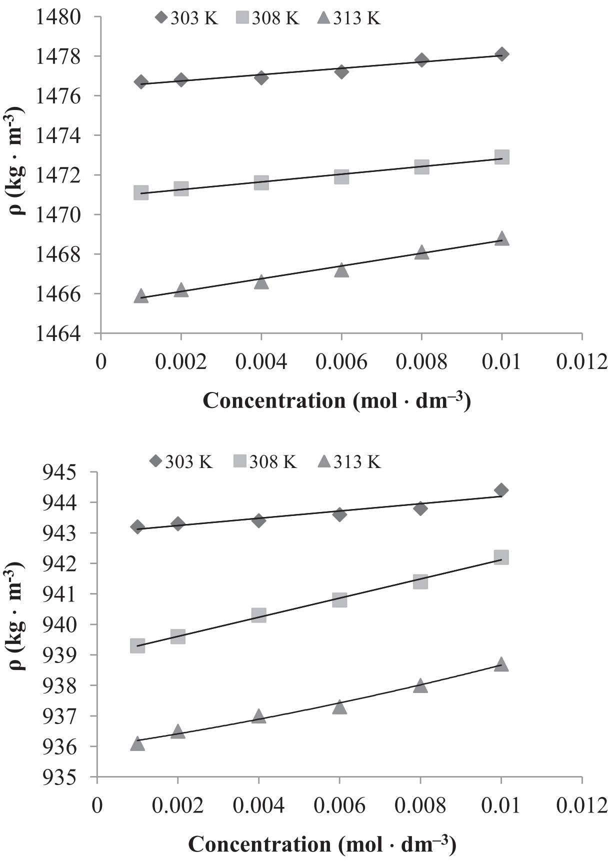

Figure 2 The plots of density (ρ) against concentration (C) for $PD_{I–C}$ in (a) CF at 303 K (♦), 308 K (■) and 313 K (▲); (b) DMF at 303 K (♦), 308 K (■) and 313 K (▲).

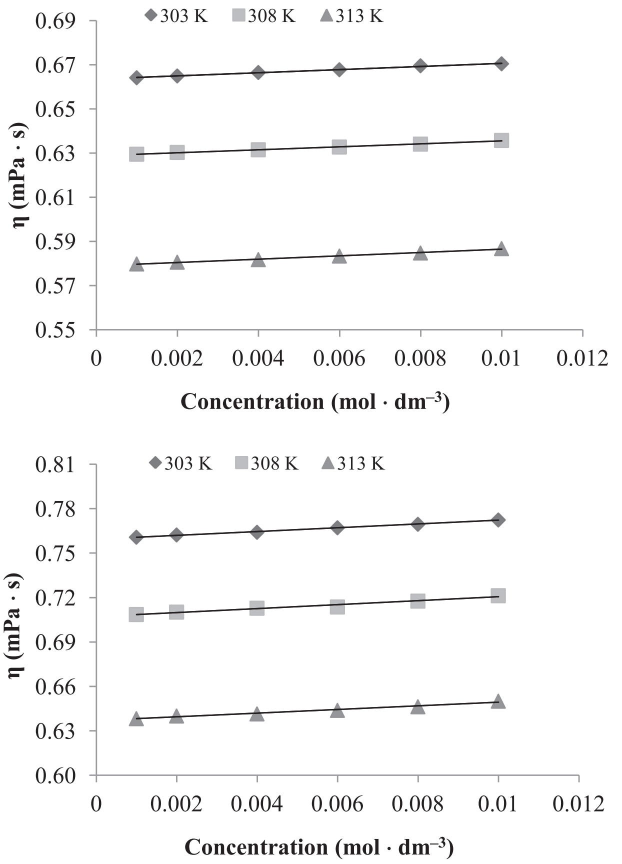

Figure 3 The plots of viscosity (η) against concentration (C) for $PD_{I–C}$ in (a) CF at 303 K (♦), 308 K (■) and 313 K (▲); (b) DMF at 303 K (♦), 308 K (■) and 313 K (▲).

and DMF at three different temperatures according to standard equations. The concentration and temperature dependence of acoustical parameters furnish a wealth of information regarding the strength of molecular interaction occurring in the solutions. Various acoustical parameters were fitted with concentration by least square analysis to certain concentration and temperature dependence molecular interactions in $PD_{I–C}$ solutions and hence the structure forming or structure-breaking nature of compound $PD_{I–C}$ is under investigation.

Ultrasonic velocity (U) depends on intermolecular free path length (L_f) inversely. It can seen from Tables 3 and 4 that, in CF and DMF systems both velocity and acoustical impendence (Z) increase with C and decrease with T of solute. The intermolecular free path length (L_f) is observed to decrease with C and increase with T suggesting the presence of solvent–solute interactions (Fig. 6).

When ultrasonic waves are incident on the solution, the molecules get perturbed. Since the medium has some elasticity and hence perturbed molecules regain their equilibrium positions. When a solute is added to a solvent, its molecules attract certain solvent molecules toward them, this phenomenon is known as compression. Every solvent has a limit for compression and is known as limiting compressibility. The decrease of adiabatic compressibility (κ_a) might be due to aggregation of solvent molecules around solute molecules supporting strong solvent–solute interactions. The adiabatic compressibility (κ_a) of the solutions of $PD_{I–C}$ was also found to decrease with C and increase with T in both systems (Fig. 5). This phenomenon can be attributed to the solvated molecules that were fully compressed by the electrical forces of the ions. The compressibility of the solution was mainly due to the free solvent molecules. The presence of compressibility of the solution decreases with the increase in solute concentration, due to solute–solvent interactions in the system. This was further confirmed by the increase in viscosity of $PD_{I–C}$ solutions in CF and DMF systems.

According to Jacobson's intermolecular free length theory for liquids, the molecules of the liquid are assumed to be spherical and the average value of the distance that the ultrasonic waves travel between the two molecules is called the intermolecular free path length. Decrease of L_f with C further supported solvent–solute interactions. Due to solvent–solute interactions, structural arrangement is considerably changed.

The linear changes in Rao's molar sound function (R_m) and Van der Waals constant (b) shown in Tables 3 and 4 (correlation coefficient $\gamma = 0.931–0.994$) suggest that the absence of any complex or aggregate formation takes place in both CF and DMF systems (except at 308 K in DMF system).

The internal pressure (π) is the resultant of forces of attraction and repulsion between the molecules in a solution. The results of adiabatic compressibility and intermolecular free path length, which were found decreased with C and increased with T, while velocity and viscosity were found increased with C

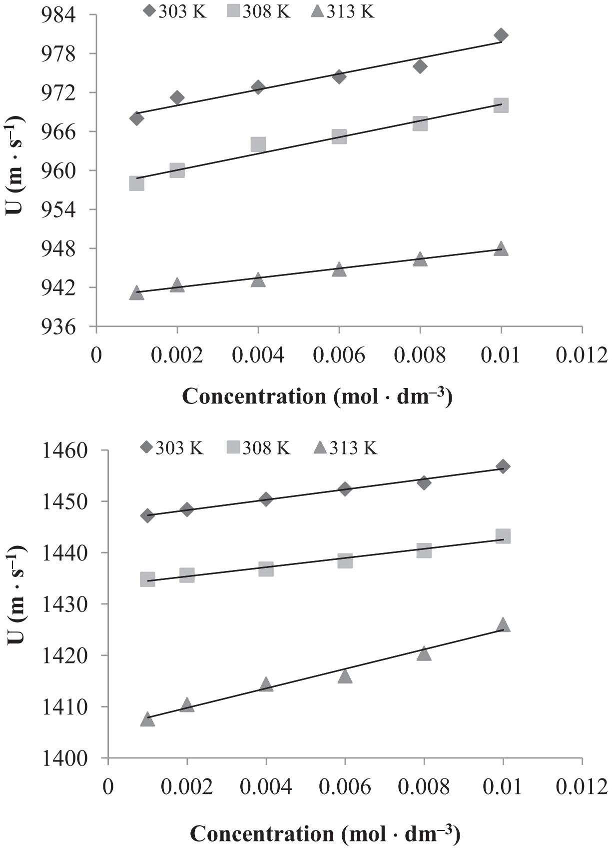

Figure 4 The plots of velocity (U) against concentration (C) for $PD_{I\text{–}C}$ in (a) CF at 303 K (◆), 308 K (■) and 313 K (▲); (b) DMF at 303 K (◆), 308 K (■) and 313 K (▲).

Table 3 The least-square equations and regression coefficients for $PD_{I\text{–}C}$ solutions in CF at 303, 308 and 313 K.

Parameter	Least square equations (regression coefficients, R^2) [CF + $PD_{I\text{–}C}$ system]		
	T = 303 K	T = 308 K	T = 313 K
ρ (kg m^{-3})	160.2C + 1476 (0.944)	194.5C + 1470 (0.986)	321.6C + 1465 (0.984)
η (mPa s)	0.717C + 0.663 (0.994)	0.672C + 0.628 (0.996)	0.752C + 0.579 (0.994)
U (m s^{-1})	1218.0C + 967.5 (0.945)	1261.0C + 957.5 (0.971)	730.9C + 940.5 (0.991)
$Z \times 10^6$ (kg m^{-2} s^{-1})	1.956C + 1.428 (0.953)	2.044C + 1.408 (0.977)	1.376C + 1.378 (0.991)
$\kappa_a \times 10^{-10}$ (Pa^{-1})	−18.60C + 7.234 (0.950)	−20.09C + 7.414 (0.973)	−13.49C + 7.713 (0.992)
$L_f \times 10^{-11}$ (m)	−7.295C + 5.631 (0.950)	−7.781C + 5.701 (0.973)	−5.112C + 5.814 (0.991)
$R_m \times 10^{-4}$(m$^{10/3}$ s$^{-1/3}$ mol^{-1})	$14267C^3 - 2353.0C^2 + 13.22C + 7.992$ (0.993)	$69352C^3 - 1345.0C^2 + 9.938C + 7.996$ (0.993)	$-41.61C^2 + 0.933C + 7.986$ (0.933)
$b \times 10^{-5}$ (m^3)	$-65.28C^2 + 0.102C + 7.960$ (0.955)	−0.794C + 7.991 (0.974)	−1.534C + 8.018 (0.980)
$\pi \times 10^8$ (Pa)	$-3E + 06C^4 - 52826C^3 + 1399.C^2 - 6.869C + 4.224$ (0.896)	$-6E+06C^4 + 96790C^3 - 173.3C^2 - 2.303C + 4.121$ (0.901)	1.561C + 4.107 (0.987)
$V_f \times 10^{-7}$ (m^3)	$20935C^3 - 3275C^2 + 14.37C + 2.585$ (0.918)	−1.468C + 2.308 (0.954)	−2.260C + 3.054 (0.979)
S_n	$-1E+07C^3 + 15520C^2 - 382.1C + 0.33$ (0.999)	$-3E+09C^4 + 5E+07C^3 - 26904C^2 + 666.4C - 0.376$ (0.988)	$-4E+12C^5 + 1E+11C^4 - 9E + 08C^3 + 3E + 06C^2 - 4500.0C + 1.911$ (1)

and decreased with T in CF and DMF systems, suggest that solute–solvent interaction is more predominant. This was confirmed from the results of internal pressure which was found to be increased. The internal pressure (π) increased with C and decreased with T in both solvent systems (except at 303 and 313 K in CF system). Internal pressure of a solution is single factor, which plays an important role in transport properties of solutions. The increase of internal pressure (π) and decrease of free volume (V_f) indicate the increase of cohesive forces and *vice versa* in the solutions of $PD_{I\text{–}C}$ in both solvent systems. The increase in internal pressure and decrease in free volume with concentration in both systems indicate ordered structural arrangement due to decreasing entropy of the system. The free volume (V_f) of a solute molecule at a particular temperature and pressure depends on the internal pressure of a liquid in which it is dissolved. The decrease in free volume causes internal pressure to increase or *vice versa*. However, Tables 3 and 4 show that the internal pressure increased and free volume decreased in both solvent systems. This again confirmed the existence of solute–solute and solute–solvent interactions in the system studied so far.

The degree of interaction was also measured in terms of solvation number (S_n). The negative solvation number indicates the structure-breaking tendency of solute (Woland, 1988). The decrease in the S_n with C suggested the presence of solute–solute interaction. The resultant value of the S_n depends upon solvent–solute and solute–solute interactions. It is clear from Tables 3 and 4 that solvation is powerful in DMF and

Table 4 The least-square equations and regression coefficients for PD_{I-C} solutions in DMF at 303, 308 and 313 K.

Parameter	Least square equations (regression coefficients, R^2) [DMF + PD_{I-C} system]		
	$T = 303$ K	$T = 308$ K	$T = 313$ K
ρ (kg m^{-3})	$119.7C + 943.0$ (0.900)	$313.9C + 938.9$ (0.996)	$-13836C^2 + 320.8C + 934.5$ (0.934)
η (mPa s)	$1.274C + 0.759$ (0.996)	$1.335C + 0.707$ (0.972)	$1.234C + 0.637$ (0.982)
U (m s^{-1})	$1008.0C + 1446.0$ (0.987)	$897.5C + 1433.0$ (0.977)	$1897.0C + 1406.0$ (0.979)
$Z \times 10^6$ (kg m^{-2} s^{-1})	$1.125C + 1.363$ (0.981)	$1.296C + 1.346$ (0.987)	$2.165C + 1.315$ (0.980)
$\kappa_a \times 10^{-10}$ (Pa^{-1})	$-7.62C + 5.069$ (0.985)	$-8.121C + 5.182$ (0.984)	$-15.78C + 5.404$ (0.980)
$L_f \times 10^{-11}$ (m)	$-3.557C + 4.714$ (0.985)	$-3.751C + 4.766$ (0.984)	$-7.168C + 4.867$ (0.980)
$R_m \times 10^{-4}$ (m$^{10/3}$ s$^{-1/3}$ mol^{-1})	$1.460C + 8.763$ (0.967)	$74.27C^2 - 1.364C + 8.776$ (0.955)	$-54526C^3 + 945.7C^2 - 2.663C + 8.754$ (0.990)
$b \times 10^{-5}$ (m^3)	$-113.4C^2 + 0.793C + 7.633$ (0.931)	$-2.026C + 7.667$ (0.994)	$-61608C^3 + 1134.0C^2 - 6.684C + 7.705$ (0.978)
$\pi \times 10^8$ (Pa)	$7E + 09C^5 - 2E + 08C^4 + 2E + 06C^3 - 9084.0C^2 + 18.49C + 4.849$ (1)	$3.640C + 4.695$ (0.969)	$1.909C + 4.637$ (0.947)
$V_f \times 10^{-7}$ (m^3)	$-2.503C + 1.854$ (0.987)	$-1.468C + 2.308$ (0.954)	$-154.2C^2 - 0.111C + 2.311$ (0.923)
S_n	$-2E + 07C^3 + 20679C^2 + 54.92C + 0.111$ (0.962)	$-89578C^2 + 1444.0C - 1.015$ (0.963)	$2E + 13C^5 - 4E + 11C^4 + 4E + 09C^3 - 2E + 07C^2 + 25724C - 13.55$ (1)

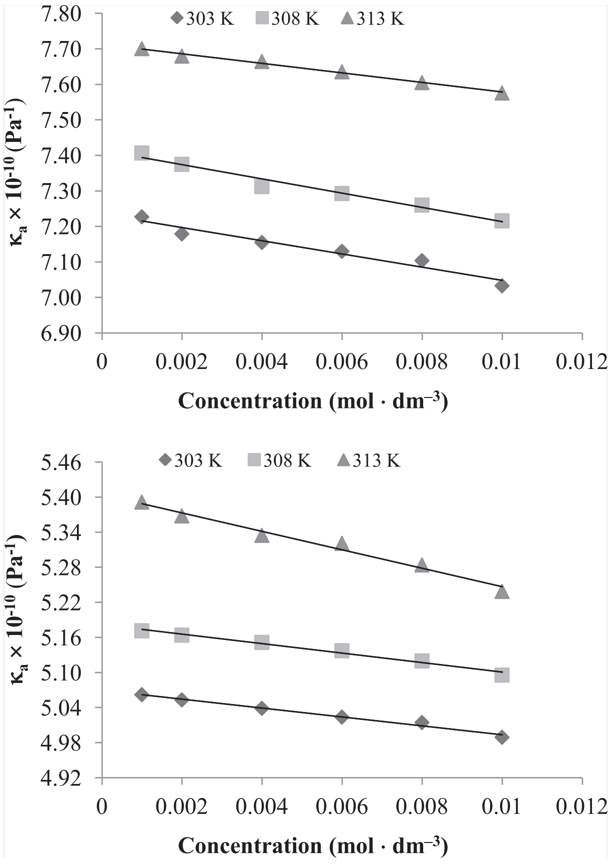

Figure 5 The plots of adiabatic compressibility (κ_a) against concentration (C) for PD_{I-C} in (a) CF at 303 K (◆), 308 K (■) and 313 K (▲); (b) DMF at 303 K (◆), 308 K (■) and 313 K (▲).

minimum in the CF system. The lone pairs and –Cl are electronegative groups whereas $-CH_3$, –OH and phenyl rings are electro positive groups. Halogen group forms weak H–bond with electropositive groups and hence solvation number was minimum in CF as compared to DMF system. It is clear from our results that S_n values are positive which shows the structure-forming tendency in CF and DMF systems. The variation in S_n with C and T values suggested the presence of strong dipole–dipole interaction. This is further suggestive that solute–solute and solute–solvent interactions are present in solution and the structure-forming tendency of PD_{I-C} in CF and DMF.

4. Conclusions

On the basis of the experimental findings, it is concluded that ρ, η and U increased with concentration and decreased with temperature in both systems. Powerful molecular interactions resulted in the structure forming as judged on the basis of positive values of the solvation number. Thus, electronegative (–Cl and lone pairs) and electropositive ($-CH_3$, –OH and phenyl rings) groups have played an important role on molecular interactions. The various thermodynamic parameters have been studied in this work; support each other and also the existence of weak and strong dispersive forces in the binary mixtures. The parameters obtained from the correlating equations have also provided us with valuable information.

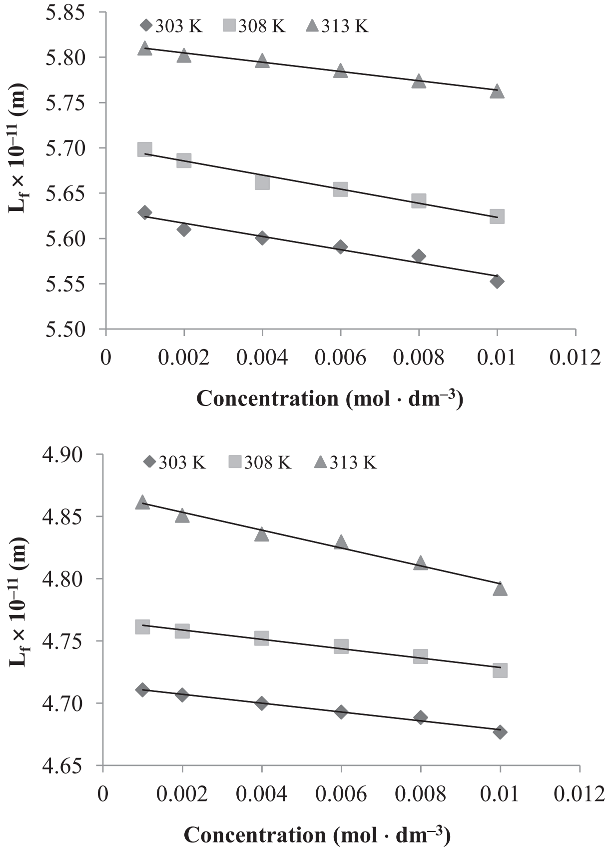

Figure 6 The plots of intermolecular free path length (L_f) against concentration (C) for $PD_{I–C}$ in (a) CF at 303 K (♦), 308 K (■) and 313 K (▲); (b) DMF at 303 K (♦), 308 K (■) and 313 K (▲).

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