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Thermo-acoustic approach for pesticide-plasma protein binding in colloidal system: An impact of membrane mimic structures on molecular interactions in biological systems

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ABSTRACT

Recently, use of agrochemicals, most importantly pesticides has experienced an enormous upsurge as a consequence of continuously increasing demand of enhanced crop production. Various toxins in the environment interact with bio-molecules and causes serious ailments in human beings. Different physicochemical, computational and spectroscopic methods have been used to study binding of toxins with bio-molecules. In present study, thermo-acoustic method was aimed to employ for studying binding of organophosphate pesticides with plasma protein in absence and presence of colloidal solutions of ionic surfactants. Role of different binding sites in protein molecules, nature of pesticide molecules and forces involved in pesticide-plasma protein binding were investigated. Volumetric and acoustic parameters such as apparent (V_ϕ) and partial molar volume (V_ϕ^o), expansibility factor (E_ϕ^o), Hepler's constant, compressibility factor (K_ϕ) and intermolecular free length (L_f) were calculated using density and sound velocity data at different temperatures (293.15–313.15)K. Positive values of V_ϕ increased with increasing pesticide concentration in aqueous plasma protein solutions which were indicative of strong associative molecular interactions in solutions. Obtained results of this study about pesticides-protein binding will be helpful for medical and pharmaceutical researchers.

1. Introduction

Globally the growing population has increased demand of food [1]. Pesticides have been used as crop protection agents to boost the agricultural production [2]. Pesticide residues can pass in the human body through different means including inhalation, ingestion and dermal penetration [3]. Due to inability of human body to metabolize these compounds; pesticides have resulted in serious health problems via interacting with bio-molecules [4]. Serum albumin interacts and solubilize various small molecules inside the body and regulate their transportation and metabolism [5]. The toxic effect of a ligand inside the human body can also be related to its binding capacity with plasma protein [6]. Therefore, protein–ligand binding studies have great significance in biomedical research [7].

During past few years, binding of plasma protein with different drugs or environmental toxins have been investigated using computational, physico-chemical and various spectroscopic methods [8–12]. As in biological system, virtually all the reactions such as binding of protein with ligand and its structural fluctuations proceed with a change in compressibility which can be evaluated from ultrasonic measurements. Most physical and chemical investigations in biological systems using acoustic methods were based on the measurement of ultrasonic absorption over a wide range of frequencies (known as ultrasonic spectroscopy) to obtain the kinetic and thermodynamic characteristics of chemical processes. Ultrasonic spectroscopy is a complementary method to ultrasonic velocimetry, although applications of the later differ greatly from those of ultrasonic spectroscopy [13]. Dispersion of ultrasonic velocity in aqueous solutions of biological substances is usually small and in many cases all acoustic information on molecular structures and interactions can be obtained using measurements at a fixed frequency. That's why ultrasonic velocimetry; which does not need frequency-dependence measurements, is preferable over ultrasonic spectroscopy in which a wide range of frequencies is required for measurements [14].

The main purpose of molecular acoustics is to study dependence of velocity and attenuation of ultrasonic waves on the molecular properties

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of substance [15]. The conformational state of bio-macromolecules in solution are reflected in the physical parameters of solution such as density, compressibility and relaxational spectra. These parameters govern acoustic behavior of the system. Changes in velocity of sound waves gives the understanding of mechanism of interactions among macromolecules and solvents molecules [16].

The two most important requirements for biomolecular studies, i.e. low cell volume and high precision has made acoustic method very valuable for studies related to biomolecular processes. Moreover, intermolecular forces responsible for the structure and thermodynamics of biological systems are highly nonlinear with respect to the distance between interacting atoms. Description of molecular interactions in terms of the values of compressibility is just a linear approximation. Nonlinearity is one of the least investigated characteristics of various kinds of molecular interactions, and it can be evaluated from the dependence of density and compressibility of a system on pressure or by measuring the ultrasonic velocity as a function of pressure [13]. Investigation of the nonlinearity of molecular interaction using ultrasonic velocity and density began only a few years ago, and it has proven to be an efficient approach in biomolecular studies.

Recently there has been a marked increase in interest in ultrasonic studies of biological systems. Much effort has been devoted in the area of study of protein folding/unfolding transitions induced by the variation in temperature, pressure, pH, cosolvent composition, ligand binding, and oxidation/reduction reactions using volumetric and acoustic studies . To best of our knowledge, no study has been reported yet about hydration and compressibility of human serum albumin in terms of organophosphate pesticides-protein interactions in micellar medium of ionic surfactants. Therefore, in present work, it was aimed to employ volumetric and acoustic methods to study binding of pesticides with plasma protein in colloidal (micellar) system providing micellar interfacial region as biological membrane mimic structures in solutions. The effect of temperature as well as pesticide's concentration on the hydration behavior of protein has also been studied from the volumetric and acoustic parameters. Obtained results may provide comprehensive valuable information about changes in the solvation/hydration shell structure of protein which has significant applications in biological and pharmaceutical fields[17]. Organo phosphate pesticides used in this study were acephate and dimethoate. Molecular structures of acephate and dimethoate are shown in Fig. 1.

2. Experimental

2.1. Chemicals

Chemicals; human serum albumin (CAS No. 70024–90-7), acephate (CAS No 30560–19-1), dimethoate (CAS No 60–51-9), sodium dodecyl sulphate (CAS No 51–21-3) and cetyltrimethyl ammonium bromide (CAS No 57–09-0) used in present study were products of Sigma Aldrich and were used as received without any further purification.

2.2. Methods

Density and sound velocity analyzer (Anto Paar DSA 5000 M) was used for density and sound velocity measurements. It has two allied cells which instantaneously measure sound wavelength and density of materials at atmospheric pressure. The accuracy and repeatability of DSA 5000 M for density measurements are 5×10^{-6} gcm^{-3} and 1×10^{-6} gcm^{-3} respectively, while for sound velocity these are 0.5 ms^{-1} and 0.1 ms^{-1} respectively. The temperature of instrument is controlled by a built-in Peltier thermostate. Accuracy in temperature is ± 0.01 K. The density of the sample is determined by measuring the oscillation frequency of a U-shaped sample tube completely filled with the sample liquid. The principle of sound velocity measurement is based upon propagation time technique. The sample is sandwiched between two piezoelectric ultrasound transducers. One transducer emits sound waves through the sample filled cavity (frequency around 3 MHz) and second transducer receives those waves. Thus, sound velocity is obtained by dividing known distance between transmitter and receiver by measured propagation time of the sound waves [18]. Weighing of sample was done using Wiggen hause electronic balance (model no. WH180-4) with a precision of ± 0.0001 g. Glassware was washed and cleaned with distilled water and dried in an oven before use. Solutions of organophosphate pesticides (acephate and dimethoate) of different concentrations were prepared in aqueous plasma protein solutions and in ionic surfactant solutions of varying concentrations (pre-micellar to post micellar concentrations). Deionized distilled H_2O was used in all solutions.

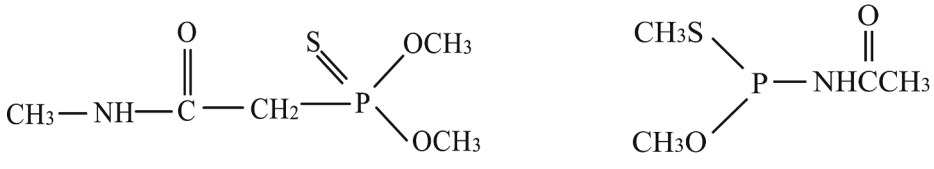
3. Results and discussion

3.1. Density and sound velocity measurements

Density is the measure of how tightly a material is packed in a system. Density of materials can be varied by a change in temperature and pressure. With increasing temperature, collisions among molecules increases making the liquid less dense [19]. Velocity of ultrasonic waves passing through solution depends upon temperature and composition of medium. Liquids undergo small, confined compressions and expansions, which resultantly changes the sound velocity in medium.

Density and sound velocity of different concentrations of organophosphate pesticides (acephate and dimethoate) in plasma protein solutions of varying concentration (20–100) μM were measured in the presence and absence of ionic surfactants (CTAB and SDS) at a temperature range of 293.15–313.15 K. Obtained data has given in Tables S1 and S2 (a & b) in supplementary information. It is clear from results that density increases with increasing concentration of organophosphate pesticides as well as of plasma protein. This increase in density at higher concentration of pesticides and plasma protein could be due to the formation of compact structure of solvent by the addition of solute (pesticides). At higher temperature, solution becomes less dense because with increasing temperature kinetic energy of molecules dominates over bonding energy of components in solution [20].

Similarly, sound velocity of solutions containing pesticides and plasma protein molecules increases with increasing concentration of pesticides in solution, which could be due to overall rise of cohesive interactions between pesticides and plasma protein molecules While at higher temperature, sound velocity of pesticides solutions decreases



(a) (b)

Fig. 1. Molecular structures of (a) dimethoate and (b) acephate.

because collision energy among solution components increases and hence molecules in solution pose hindrance to the passage of sound waves [21].

Reported data showed that among both organophosphate pesticides (acephate and dimethoate), greater magnitude of density and sound velocity values in aqueous plasma protein solutions were found for acephate than for dimethoate because P═S of dimethoate is less solvated (less electrostatic attractions) than P═O of acephate because P═O is molar polar as compared to P═S, due to electronegativity difference (electronegativity of oxygen is 3.44 while for sulphur it is 2.58). As greater the difference in electronegativity, more polarized the electron distribution and larger the partial charges of atoms.

In the presence of ionic surfactants (CTAB and SDS) at their pre and post micellar concentrations, density and sound velocity for pesticides solutions increase with increasing concentrations of organophosphate pesticides. This indicated formation of more compressed structure of organophosphate pesticides and amphiphilic substances in solutions [20]. Moreover, density decreases with temperature because with increasing temperature thermal energy between pesticide and solvent molecules increases than binding energy among molecules due to which bond become weaker and solution becomes less dense [22]. Similarly, ultrasonic velocity of all solutions increases at higher concentration of pesticides due to cohesion interaction among surfactant and organophosphate pesticide molecules in solutions. In the presence of ionic surfactants binding of pesticides with plasma protein decreased because more electrostatic interactions were present among pesticides and hydrophilic head groups and hydrophobic chain of surfactant molecules. Resultantly, very small number of pesticide molecules could approach to plasma protein (human serum album). Among both ionic surfactants, density and sound velocity of organophosphate pesticide's solutions is higher in the case of cationic surfactant (CTAB) than anionic surfactant (SDS) because CTAB develop stronger molecular interactions with negatively charge carrying species (P═O and P═S) present in pesticide molecules in solutions. On the other hand, anionic head group of surfactant molecules face repulsion with negatively charged carrying species present in solutions.

3.2. Volumetric parameters

3.2.1. Apparent molar volume (V_ϕ)

Apparent molar volume (V_ϕ) gives a description of the molecule's total volume by real measurement of solvated molecules in solution. As a result, the volume of solution becomes greater than its molecular volume. This is due to formation of hydrogen bond between water molecules and solute preventing a direct interaction of solute with its neighboring solvent molecules in solution. The contributions from intrinsic volume of solute, volume from solute-solute and solute–solvent interactions together form the apparent molar volume [21]. In present experiment, apparent molar volume of organophosphate pesticides (acephate and dimethoate) and plasma protein (human serum albumin; HSA) in aqueous solutions and colloidal medium of ionic surfactants was calculated using following mathematical equation [23].

$$V_\phi = M/d - [1000(d - d_o)/mdd_o] \quad (1)$$

Where, M is molar mass of solute (acephate; 183.2 g.mol^{-1} and dimethoate; 229.26 g.mol^{-1}), m represents solution concentration in molality, d and d_o denote density of solution and solvent respectively. Graphical presentation of variation of apparent molar volume with molality of pesticide's solutions in 20 × 10^{-6} mol.kg^{-1} HSA at different temperatures 293.15–313.15 K is shown in Figs. 2 and 3. Similar trend is observed for other concentrations of HSA in the absence and presence of ionic surfactants as obvious from data given in supplementary information (Figs. S1-S16).

From data, it is obvious that the values of apparent molar volume are positive and increase with increasing concentration of pesticides at respective temperatures. Positive V_ϕ values are indicative of strong

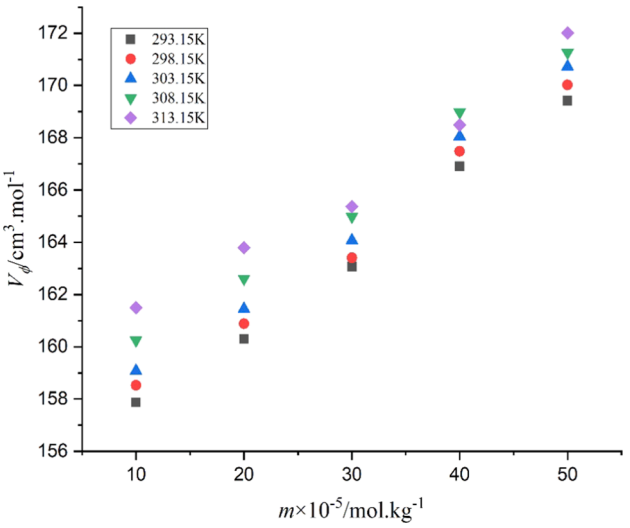


Fig. 2. Graphical presentation of variation of apparent molar volume (V_ϕ) with molality (m) of acephate solutions in 20 × 10^{-6} mol.kg^{-1} HSA at different temperatures.

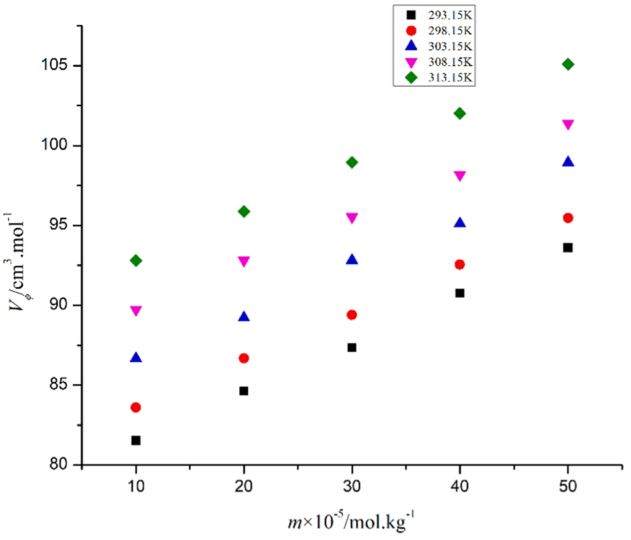


Fig. 3. Graphical presentation of variation of apparent molar volume (V_ϕ) with molality (m) of dimethoate solutions in 20 × 10^{-6} mol.kg^{-1} HSA at different temperatures.

molecular interactions in solutions. With increasing concentration of pesticides molecules, a greater number of pesticide molecules become available to interact with solvent molecules (aqueous plasma protein solutions of different concentrations). Possible molecular interactions present among active species of pesticides and plasma protein are electrostatic interactions, multiple hydrogen bonds, weak van der Waals forces and hydrophobic interactions [24]. Backbone of protein consists of a single polypeptide chain of 585 amino acid residues which form three homologous domains (I, II, and III), stabilized by 17 disulfide bridges due to 34 cysteines present in molecule; each domain contains two subdomains (A and B), respectively constituted by 6 and 4 α-helices [25]. Both hydrophobic and electrostatic interactions play a major role in controlling the affinity towards binding sites I and II [26]. For site I, mainly hydrophobic interactions are dominant, while for site II, a combination of hydrophobic, hydrogen bonding and electrostatic interactions play a crucial role. When any foreign molecule binds to one domain, it can induce conformational changes on the other domain, as both subdomains share a common interface. For this reason, the binding

Table 1
Partial molar volume (V_ϕ^o) of acephate and dimethoate in aqueous plasma protein and in ionic surfactant solutions at different temperatures (T).

V_ϕ^o /cm^3.mol^{-1}				
In Acephate				
293.15 K	**298.15 K**	**303.15 K**	**308.15 K**	**313.15 K**
20 × 10^{-6} mol.kg^{-1} HSA				
129.82	131.20	131.87	132.20	132.77
40 × 10^{-6} mol.kg^{-1} HSA				
139.97	140.16	140.61	140.76	140.98
60 × 10^{-6} mol.kg^{-1} HSA				
140.82	141.50	142.06	142.26	142.55
80 × 10^{-6} mol.kg^{-1} HSA				
142.52	144.30	144.50	145.09	145.29
100 × 10^{-6} mol.kg^{-1} HSA				
145.12	145.78	147.94	149.67	151.44
5.4 × 10^{-4} mol.kg^{-1} CTAB + 100 × 10^{-6} mol.kg^{-1} HSA				
153.08	153.86	155.01	155.47	155.48
22.5 × 10^{-4} mol.kg^{-1} CTAB + 100 × 10^{-6} mol.kg^{-1} HSA				
165.30	166.13	166.61	167.41	169.18
4.7 × 10^{-3} mol.kg^{-1} SDS + 100 × 10^{-6} mol.kg^{-1} HSA				
162.78	163.59	165.28	170.71	171.59
15.2 × 10^{-3} mol.kg^{-1} SDS + 100 × 10^{-6} mol.kg^{-1} HSA				
170.35	171.25	171.79	173.03	175.62
In Dimethoate				
293.15 K	**298.15 K**	**303.15 K**	**308.15 K**	**313.15 K**
20 × 10^{-6} mol.kg^{-1} HSA				
78.494	80.650	83.422	86.927	89.744
40 × 10^{-6} mol.kg^{-1} HSA				
87.88	92.65	95.81	99.95	102.58
60 × 10^{-6} mol.kg^{-1} HSA				
93.93	97.077	101.33	105.67	109.89
80 × 10^{-6} mol.kg^{-1} HSA				
96.914	101.42	105.23	109.19	113.66
100 × 10^{-6} mol.kg^{-1} HSA				
102.05	106.13	110.51	114.25	118.84
5.4 × 10^{-4} mol.kg^{-1} CTAB + 100 × 10^{-6} mol.kg^{-1} HSA				
161.44	165.19	168.19	173.06	176.77
22.5 × 10^{-4} mol.kg^{-1} CTAB + 100 × 10^{-6} mol.kg^{-1} HSA				
158.61	161.86	166.53	170.45	174.8
4.7 × 10^{-3} mol.kg^{-1} SDS + 100 × 10^{-6} mol.kg^{-1} HSA				
138.31	142.66	146.73	150.59	154.46
15.2 × 10^{-3} mol.kg^{-1} SDS + 100 × 10^{-6} mol.kg^{-1} HSA				
135.62	139.98	142.08	144.95	150.34

of a drug to serum albumin may change considerably the binding abilities of HSA towards other molecules [27,28].

Hydrophobic interactions among hydrophobic groups of acephate and dimethoate molecules with hydrophobic moiety of plasma protein molecules occur mostly in site I of plasma protein. While electrostatic interactions among polar groups in pesticide molecules (—C═O, —NH, —P═O, P—S) and active sites of plasma protein occur with binding site II of plasma protein. Among the two organophosphate pesticides, acephate due to greater electronegativity difference in its charged/polar moieties develop stronger interactions with plasma protein than dimethoate which have comparatively lower electronegativity difference.

Surfactant micelles mimic the biological membranes across which any toxic material enter into blood stream. Presence of ionic surfactants (CTAB and SDS) in studied system causes an increased extent of molecular interactions in solutions. Magnitude of apparent molar volume values is greater in colloidal system as compared to those in aqueous solutions. In general, following types of interactions are expected to be operative in the present systems [29].

i. Ion–ion interactions between charged species of pesticide molecules (—NH, P═S, C═O, —OCH_3) and —N^+ $(CH_3)_3$ and Br^- ions of CTAB or -OSO_3^- and Na^+ ions of SDS in the respective systems. However, the interaction between active sites of plasma protein (disulphide bridges, amino acid residues, hydrophobic interactions in binding site I, hydrogen bonding, electrostatic interactions at binding site II) and pesticides is present in all solutions.
ii. Ion–hydrophilic interactions between hydrophilic head groups of surfactant molecules on the surface of ionic micelles in water and charged moities in pesticide molecules (—NH, P═S, C═O, —OCH_3).
iii. Ion-hydrophobic interactions between ionic head groups of surfactants and hydrophobic groups in pesticide molecules (—CH_3, ═CH_2).
iv. Hydrophilic- hydrophobic interactions between the hydrophilic sites in pesticide molecules and the alkyl chains of ionic surfactant molecules.
v. Hydrophobic–hydrophobic interactions between alkyl chains of surfactant molecules and non-polar sites of pesticide molecules.
vi. Hydrogen bonding among surfactant molecules, pesticides, and aqueous plasma protein solutions.

Increase in V_ϕ values at pre-micellar concentration of surfactants is due to predominance of ion-ion interactions between head groups of ionic surfactant molecules in monomeric form in solutions and charged moieties in pesticide molecules. As a result, very less number of pesticide molecules become available for binding with plasma protein. While at post micellar concentration of surfactants, electrostatic charge is present on micellar surface of both ionic surfactants. Due to head group repulsions, charged moieties of pesticide molecules get associated themselves among ionic head groups of surfactant molecules. Some pesticide molecules could also get inserted into hydrophobic core of surfactant

Table 2
Limiting apparent molar expansibility (E_ϕ^o) and Hepler's constant ($\partial E_\phi^o/\partial T$) for acephate in aqueous plasma protein and in the presence of ionic surfactants of different concentrations at different temperatures (T).

Solutions	E_ϕ^o/cm^3 mol^{-1} K^{-1}					$\partial E_\phi^o/\partial T$ / cm^3 mol^{-1} K^{-2}
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	
20×10^{-6} mol.kg^{-1} HSA	6.8165	6.8725	6.9285	6.9845	7.0405	0.0112
40×10^{-6} mol.kg^{-1} HSA	0.8784	0.8854	0.8924	0.8994	0.9064	0.0014
60×10^{-6} mol.kg^{-1} HSA	5.3398	5.3838	5.4278	5.4718	5.5158	0.0088
80×10^{-6} mol.kg^{-1} HSA	6.8545	6.9275	7.0005	7.0735	7.1465	0.0099
100×10^{-6} mol.kg^{-1} HSA	5.7603	5.8113	5.8623	5.9133	5.9643	0.0102
5.4×10^{-4} mol.kg^{-1} CTAB + 100×10^{-6} mol.kg^{-1} HSA	7.7435	7.8075	7.8715	7.9355	7.9995	0.0128
22.5×10^{-4} mol.kg^{-1} CTAB + 100×10^{-6} mol.kg^{-1} HSA	7.3238	73,868	7.4498	7.5128	7.5578	0.0126
4.7×10^{-3} mol.kg^{-1} SDS + 100×10^{-6} mol.kg^{-1} HSA	12.734	12.845	12.956	13.067	13.178	0.0111
15.2×10^{-3} mol.kg^{-1} SDS + 100×10^{-6} mol.kg^{-1} HSA	11.574	11.673	11.772	11.871	11.970	0.0198

The standard uncertainties in Limiting apparent molar expansion (E_ϕ^o), temperature (T) and pressure (P) are ± 0.008 cm^3 mol^{-1} K^{-1}, ±10^{-2} K and ± 5 kPa respectively.

micelles via ion-hydrophobic and hydrophobic-hydrophobic interactions. Due to existence of possible interactive forces (i.e. ion-hydrophilic, ion-hydrophobic and electrostatic forces) pesticide molecules showed maximum interactions with surfactant micelles and very less number of free pesticide molecules could cross the plasma membrane barrier to bind with HSA molecules. Among the two ionic surfactants, V_ϕ values are greater for cationic surfactant (CTAB) than for anionic surfactant (SDS). Because in former case, positive charge on micellar surface of CATB tend to develop strong electrostatic interactions with negatively charged carrying moieties (—NH, P═S, C═O, —OCH_3) in pesticide molecules. While in later case, anionic micellar surface of SDS develop repulsive forces with charged moieties of pesticides. In this case hydrophobic interactions play dominant role.

With increasing temperature, kinetic energy of molecules increases and dominates over binding energy of molecules [30]. Water from second solvation layer of solute molecules releases [31]. Resultantly, stronger molecular interactions between pesticide and plasma protein molecules develop. In the presence of ionic surfactants, at higher temperature, when water releases from solvation layer of pesticide molecules, amount of bulk solvent decreases causing to decrease the compression, indicating presence of stronger molecular interactions between surfactants and pesticide molecules [32].

3.2.2. Partial molar volume

Apparent molar volume at infinite dilution is known as partial molar volume or limiting values of apparent molar volume (V_ϕ^o). V_ϕ^o is obtained by plotting a graph between concentration of solution in molality (m) and apparent molar volume (V_ϕ) of pesticide solutions at respective temperatures. Values of V_ϕ^o are obtained using following Masson's equation [23].

$$V_\phi = V_\phi^o + S_v m \tag{2}$$

At infinite dilution, solute molecules are far away from each other and solute–solute interactions are negligible. Therefore, partial molar volume is the measure of solute–solvent interactions. S_v is the experimental slope and gives information about pairwise or solute–solute interactions, which are almost negligible. Obtained values of V_ϕ^o for organophosphate pesticides in aqueous plasma protein and in presence of ionic surfactants (CTAB and SDS) at different temperatures have given in Table 1. Values of S_v for both pesticides have given in Table S3 in supplementary information.

The standard uncertainties in partial molar volume (V_ϕ^o), temperature (T) and pressure (P) are ± 0.77 cm^3 mol^{-1}, ±10^{-2} K and ± 5 kPa respectively.

Variation in the values of partial molar volume with increasing temperature or concentration of aqueous plasma protein solutions could be explained on the basis of partial molar volume which is sum of two quantities as shown in following equation [33].

$$V_\phi^o = V_\phi^o(int) + V_\phi^o(elect) \tag{3}$$

Where V_ϕ^o (int) is the intrinsic apparent molar volume and V_ϕ^o (elect) is the electrostriction apparent molar volume due to solvation of solute molecule (pesticides). V_ϕ^o (int.) is the combination of two terms, van der waals forces and volume due to packing effects. V_ϕ^o (int.) contributes negligibly to overall temperature dependence. An increase in V_ϕ^o values for pesticides in aqueous plasma protein solutions with increasing temperature has been observed which could be due to releasing of second solvation layer of solvent around pesticide molecules due to high degree of thermal agitation at higher temperature which causes an increase in V_ϕ^o values [34]. With increasing concentration of plasma protein in solutions, V_ϕ^o values also increase because more number of plasma protein molecules become available for pesticides molecules to interact after release of water molecules from solvation layer of solute molecules. Among the two organophosphate pesticides, V_ϕ^o values are greater in magnitude for acephate than for dimethoate, which may be due to greater electronegativity difference among atoms (P═O) of acephate molecules and their greater polarity as compared to dimethoate molecules (P═S). Hence, the former develops strong electrostatic interactions with binding site II of plasma protein where electrostatic interactions are dominant.

In the presence of ionic surfactants, magnitude of V_ϕ^o is greater for pesticides-plasma protein solutions than in absence of surfactants. This can be explained on the basis of following types of interactions, which affect the V_ϕ^o (elec) values.

- Ions (from dissociation of surfactant molecules) – dipole (from pesticide molecules) interactions
- Hydrogen bond formation between active sites (binding site II) of plasma protein, charged groups in pesticide molecules and ionic head groups of surfactants.

Values of V_ϕ^o (int) present van der Waals forces and volume raise from molecular packaging in solutions [35]. Among the two ionic surfactants; CTAB developed stronger interactions than SDS, this can also be explained by the fact that higher value of molar mass leads to higher values of partial molar volume. (For SDS, molar mass is 288.372 g. mol^{-1}, while for CTAB it is 364.45 g.mol^{-1}. This difference may be aroused from the electrostriction contribution. Stronger pesticides-surfactant interactions could raise volume due to molecular packaging effect in solution [36].

3.2.3. Partial molar expansibility

Partial molar expansibility, an important volumetric parameter which indicates the extent of solute–solvent interactions and also about structure making or breaking behavior of solutes in solutions. Variation of V_ϕ^o with temperature is being expressed by following polynomial equation [24].

$$V_\phi^o = a + bT + cT^2 \tag{4}$$

Table 3
Limiting apparent molar expansibility (E_ϕ^o) and Hepler's constant ($\partial E_\phi^o/\partial T$) for dimethoate in aqueous plasma protein and in the presence of ionic surfactants of different concentrations at different temperatures (T).

Solutions	E_ϕ^o/cm^3 mol^{-1} K^{-1}					$\partial E_\phi^o/\partial T$ / cm^3 mol^{-1} K^{-2}
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	
20×10^{-6} mol.kg^{-1} HSA	0.092	0.354	0.616	0.878	1.140	0.0398
40×10^{-6} mol.kg^{-1} HSA	0.225	0.327	0.417	0.535	0.645	0.030
60×10^{-6} mol.kg^{-1} HSA	0.350	0.499	0.648	0.797	0.946	0.0568
80×10^{-6} mol.kg^{-1} HSA	0.406	0.435	0.568	0.684	0.777	0.0529
100×10^{-6} mol.kg^{-1} HSA	0.423	0.558	0.693	0.828	0.963	0.0623
5.4×10^{-4} mol.kg^{-1} CTAB + 100×10^{-6} mol.kg^{-1} HSA	0.584	0.651	0.734	0.884	0.998	0.0635
22.5×10^{-4} mol.kg^{-1} CTAB + 100×10^{-6} mol.kg^{-1} HSA	0.564	0.684	0.789	0.799	0.809	0.0788
4.7×10^{-3} mol.kg^{-1} SDS + 100×10^{-6} mol.kg^{-1} HSA	0.513	0.536	0.645	0.656	0.779	0.0623
15.2×10^{-3} mol.kg^{-1} SDS + 100×10^{-6} mol.kg^{-1} HSA	0.483	0.661	0.839	1.017	1.223	0.0768

The standard uncertainties in Limiting apparent molar expansion (E_ϕ^o), temperature (T) and pressure (P) are ± 0.008 cm^3 mol^{-1} K^{-1}, $\pm 10^{-2}$ K and ± 5 kPa respectively.

Partial molar expansibility (E_ϕ^o) has been calculated using following relation.

$$E_\phi^o = \left(\frac{\partial V_\phi^0}{\partial T}\right)_\rho \tag{5}$$

The limiting molar expansibility comprises of to two major components.

$$E_\phi^o = E_\phi^o(\text{electrostriction effect}) + E_\phi^o(\text{structural effect}) \tag{6}$$

The terms $\left(\frac{\partial V_\phi^0}{\partial T}\right)_\rho$ and E_ϕ^o are partial molar expansibility which gives quantitative knowledge about molecular interactions in solutions. The values of E_ϕ^o for pesticides in aqueous plasma protein solutions and in the presence of ionic surfactants are given in Tables 2 and 3.

Results show that E_ϕ^o values for both pesticides in aqueous plasma protein solutions are positive which increases with increasing temperature and plasma protein concentration. Because at higher temperature, due to release of water molecules from second solvation layer of solute (pesticides) into bulk, expansion in volume of solution occurs and resultantly charged moieties (P═S, P═S, C═O, —NH, —OCH_3) in pesticide molecules were available to develop strong electrostatic interactions with active sites (disulfide bridges and charged species of amino acid (tryptophan, tyrosine, cysteine etc. in binding site I and II) of plasma protein. E_ϕ^o values for pesticide –plasma protein solutions are greater in the presence of both ionic surfactants (CTAB and SDS) as compared to their aqueous solutions. Because at pre-micellar concentrations, surfactant monomers develop a competition with plasma protein active species to interact with charged moieties in pesticide molecules. Resultantly electrostatic associative attractions develop among hydrophilic head groups of surfactant molecules and charged moieties in pesticide molecules. While at post micellar concentration, surfactant molecules form micelles and due to presence of concentrated accumulated electrostatic charges in micellar layer/palisade layer, pesticide molecules show more strong interactions with surfactant micelles. Also ion- hydrophobic interactions occur when pesticide molecules penetrates towards hydrophobic core of micelles. Moreover, E_ϕ^o values are greater in the presence of CATB molecules than in the presence of SDS molecules. Because cationic head group (—N^+— $(CH_3)_3$) of CTAB develops strong electrostatic interactions with negatively charge carrying specie (P═S, P═S, C═O, —NH^-, —OCH_3)in pesticide molecules, while anionic head groups of SDS molecules face repulsions with negatively charge carrying species present in pesticide solutions [37].

3.2.4. Hepler's constant

The derivatives of the partial molar expansibility with temperature reflect the hydrophobicity of the solute. Hepler's proposed a method by which quantitative information on hydration of a solute can be obtained from thermal expansion of aqueous solutions using following thermodynamic relation [38].

$$\frac{\partial E_\phi^o}{\partial T} = \left(\partial^2 \cdot \frac{\partial^2 V_\phi^0}{\partial^2 T}\right)_\rho = 2c \tag{7}$$

The sign of Hepler's constant value indicates the ability of solute molecules as a structure maker or structure breaker in solutions. Positive values show the structure making ability of solutes, whereas negative values indicate structure breaking behavior of solutes in solutions. Calculated values of Hepler's constant for both organophosphate pesticides (acephate and dimethoate) in aqueous plasma protein solutions and in the presence of ionic surfactants (SDS and CTAB) have been given in Tables 2 &3. From results it is obvious that values of Hepler's constant are positive and indicating structure making behavior of pesticides in aqueous plasma protein as well as in the presence of ionic surfactants (CTAB and SDS) too [20].

3.3. Acoustic parameters

3.3.1. Apparent molar isentropic compressibility

The extent to which ions in a solution can be compressed is known as apparent molar isentropic compressibility (K_ϕ). Isentropic compressibility is a compute of inner pressure due to interactions between solute and solvent forming high compressed surroundings. This is an acoustic parameter and can be calculated using measured data of density and sound velocity for solutions. Following mathematical equation is used for calculation of K_ϕ [19].

$$K_\phi = \frac{1000(\beta_s d_o - \beta_s^o d)}{mdd_o} + \frac{\beta_s M}{d} \tag{8}$$

Where, M is molar mas of organophosphate pesticides (183.2 g. mol^{-1} for acephate and 229.26 g.mol^{-1} for dimethoate), m is molality of pesticides solutions, d_o and d the densities of solvent and solution respectively, β_s and β_s^o represent adiabatic compressibility of solution and solvent respectively. Adiabatic compressibility is obtained using following equation [21].

$$\beta_s = \left[u^2 d\right]^{-1} \tag{9}$$

Calculated values of K_ϕ for both organophosphate pesticides in aqueous plasma protein solutions of varying concentrations and in the presence of ionic surfactants (CTAB and SDS) at different temperatures 293.15 K-313.15 K have given in Tables S4 (a & b) in supplementary information.

Reported data showed that K_ϕ values are negative in magnitude indicating that solvent molecules surrounding the solute would present greater resistance to compression than in bulk, which also indicate greater loss of structural compressibility of solvent involving a greater ordering effect by solute on solvent in solution. With increasing temperature and concentration of pesticide molecules in solutions, K_ϕ values become less negative. With increasing temperature, electrostriction

Table 4
Partial molar isentropic compressibility (K_ϕ^o) of acephate and dimethoate in aqueous plasma protein and in ionic surfactant solutions at different temperatures (T).

$K_\phi^o \times 10^{-4}$/ cm^3 mol^{-1} Pa^{-1}				
In Acephate				
293.15 K	**298.15 K**	**303.15 K**	**308.15 K**	**313.15 K**
20 × 10^{-6} mol.kg^{-1} HSA				
−9.260	−9.256	−9.241	−9.125	−9.095
40 × 10^{-6} mol.kg^{-1} HSA				
−8.515	−8.450	−8.418	−8.390	−8.354
60 × 10^{-6} mol.kg^{-1} HSA				
−8.491	−8.357	−8.318	−8.293	−8.191
80 × 10^{-6} mol.kg^{-1} HSA				
−7.775	−7.725	−7.683	−7.649	−7.590
100 × 10^{-6} mol.kg^{-1} HSA				
−7.323	−7.257	−7.216	−7.173	−7.149
5.4 × 10^{-4} mol.kg^{-1} CTAB + 100 × 10^{-6} mol.kg^{-1} HSA				
−4.465	−4.431	−4.386	−4.369	−4.272
22.5 × 10^{-4} mol.kg^{-1} CTAB + 100 × 10^{-6} mol.kg^{-1} HSA				
−5.652	−5.619	−5.581	−5.490	−5.359
4.7 × 10^{-3} mol.kg^{-1} SDS + 100 × 10^{-6} mol.kg^{-1} HSA				
−6.504	−6.470	−6.449	−6.402	−6.385
15.2 × 10^{-3} mol.kg^{-1} SDS + 100 × 10^{-6} mol.kg^{-1} HSA				
−6.517	−6.496	−6.454	−6.386	−6.284
In Dimethoate				
293.15 K	**298.15 K**	**303.15 K**	**308.15 K**	**313.15 K**
20 × 10^{-6} mol.kg^{-1} HSA				
−9.998	−9.867	−9.890	−9.677	−9.354
40 × 10^{-6} mol.kg^{-1} HSA				
−9.985	−9.818	−9.611	−9.405	−9.197
60 × 10^{-6} mol.kg^{-1} HSA				
−9.948	−9.778	−9.598	−9.368	−9.018
80 × 10^{-6} mol.kg^{-1} HSA				
−9.767	−9.658	−9.487	−9.291	−8.977
100 × 10^{-6} mol.kg^{-1} HSA				
−8.751	−8.672	−8.965	−8.975	−7.873
5.4 × 10^{-4} mol.kg^{-1} CTAB + 100 × 10^{-6} mol.kg^{-1} HSA				
−3.534	−3.512	−3.498	−3.467	−3.434
22.5 × 10^{-4} mol.kg^{-1} CTAB + 100 × 10^{-6} mol.kg^{-1} HSA				
−3.6089	−3.5763	−3.5345	−3.5167	−3.4723
4.7 × 10^{-3} mol.kg^{-1} SDS + 100 × 10^{-6} mol.kg^{-1} HSA				
−3.634	−3.589	−3.562	−3.489	−3.376
15.2 × 10^{-3} mol.kg^{-1} SDS + 100 × 10^{-6} mol.kg^{-1} HSA				
−3.965	−3.783	−6.453	−5.401	−4.234

The standard uncertainties in partial molar isentropic compression (K_ϕ^o), temperature (T) and pressure (P) are ± 0.35 × 10^{-4} cm^3 mol^{-1} Pa^{-1}, ±10^{-2} K and ±5 kPa respectively.

reduces and therefore some solvent molecules are released into the bulk, thereby making the solution more compressible. Similarly, at higher concentration of pesticides, extent of molecular interactions in solutions increases because more number of charged moieties of pesticide molecules become available to interact with plasma protein. As a result solution become more compressible and strong molecular interactions prevail among solution components [21].

In the presence of ionic surfactants, apparent molar compressibility (K_ϕ) of pesticide-plasma protein solutions become less negative as compared to their aqueous solutions. This is explained on the basis of following two major factors.

i. Compressibility of the hydrophobic core of surfactant micelles
ii. Interactions between pesticide molecules and ionic head groups of the surfactant micelles.

In addition, K_ϕ is also dependent on the variation of counter ion binding and hydrophilicity of the head group [35]. From results, it is manifested that from pre micellar to post micellar concentration of both ionic surfactants, the apparent molar isentropic compressibility (K_ϕ) value decreases and becomes almost constant above CMC. In pre-micellar region, due to strong molecular interactions among hydrophilic head groups of ionic surfactant molecules and charged moieties of pesticide molecules in solutions is more compressible while rise in K_ϕ values at post micellar concentration of surfactants suggests the solvation of pesticide molecules in micelles which causes an increase in the size of micelles and reflects a reduction in inter-head group forces making the solution compressible. More compressible system tends to have negative K_ϕ values and stronger molecular interactions.

3.3.2. *Partial molar isentropic compressibility*

Apparent molar isentropic compressibility at infinite dilution is known as partial molar isentropic compressibility (K_ϕ^o). Values of K_ϕ^o have been calculated using Masson equation by extra plotting graph between molality and apparent molar isentropic compressibility of pesticide-plasma protein aqueous solutions [36].

$$K_\phi = K_\phi^o + S_k m \tag{10}$$

Obtained values of K_ϕ^o for both pesticides in aqueous plasma protein solutions and in the presence of ionic surfactants have given in Table 4. S_k values haven given in Table S5 in supplementary information.

S_k is the experimental slope indicative of pairwise or solute–solute interactions which at infinite dilution are negligible. From data given in Table 4, it is clear that K_ϕ^o values become less negative with increasing concentration of plasma protein and increase with increasing temperature. At higher temperature due to greater degree of dehydration, water molecules surrounding the solute (organophosphate pesticides) are more compressible than in bulk. Resultantly, greater degree of compression and strong molecular interactions in solution are observed. Among the two organophosphate pesticides, K_ϕ^o values are less negative

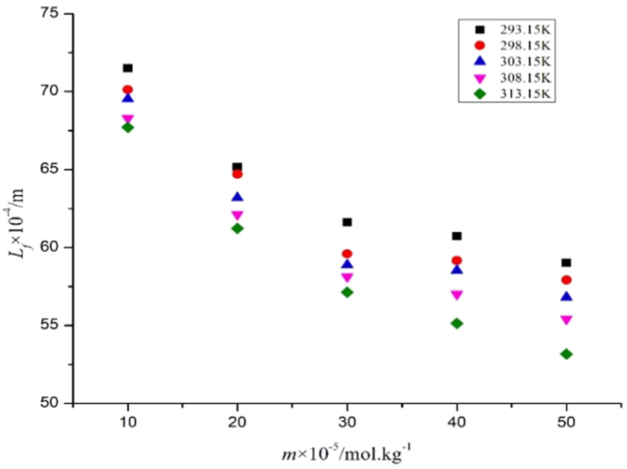


Fig. 4. Graphical presentation of variation of intermolecular free length (L_f) with molality (m) of acephate solutions in 20 × 10^{-6} mol.kg^{-1} HSA at different temperatures.

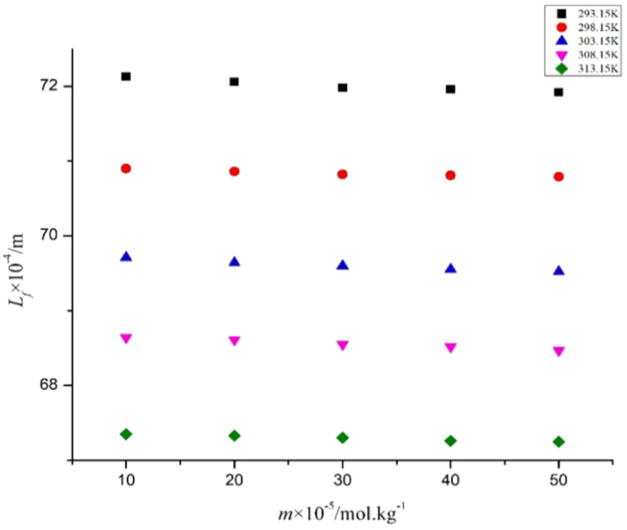


Fig. 5. Graphical presentation of variation of intermolecular free length (L_f) with molality (m) of dimethoate solutions in 20 × 10^{-6} mol.kg^{-1} HSA at different temperatures.

for acephate than for dimethoate, suggesting greater compression of solvent molecules around acephate molecules showing strong polarity in molecules due to greater electronegativity difference among atoms (C and S) in acephate molecules. Greater compression and less negative K_ϕ^o values are indicative of strong associative molecular interactions among molecules in solutions [18]. In the presence of ionic surfactants, ionic head groups of surfactant molecules and active sites of plasma protein develop competition to interact with pesticides molecules. Magnitude of K_ϕ^o values for pesticide-plasma protein solutions become less negative indicating greater compression in the presence of surfactant molecules due to strong electrostatic attractions among hydrophilic head groups of surfactant molecules and charged species in pesticide molecules. While at post micellar concentration, where surfactants are present in micellar form, pesticide molecules are supposed to be partially solvated into hydrophobic core of micelles where electrostatic attractions also develop among charged moieties of pesticide molecules and palisade layer (concentrated head groups of surfactant molecules) at interfacial surface of micelles [10]. Due to strong interactions among pesticides and surfactants; binding of pesticides with plasma protein is lowered, thus could reduce toxic effects of pesticides on plasma protein structure.

3.3.3. *Intermolecular free length (L_f)*

Intermolecular free length (L_f) depends on molecular interactions among different species and is the distance between the surfaces of neighboring molecules. The experimental values of isentropic compression (β_s) were further utilized to calculate the intermolecular free length (L_f) using following mathematical relation [39].

$$L_f = K(\beta_s)^{1/2} \tag{11}$$

K is a constant which depends on temperature and is equal to 93.875 + 0.375 T × 10^{-8} with T as absolute temperature. Calculated values of intermolecular free length for organophosphate pesticides in aqueous plasma protein solutions in the absence and presence of ionic surfactants have given in Tables S6 (a & b) in supplementary information. Graphical presentation of variation of L_f with molality (m) of pesticides (acephate and dimethoate) in aqueous HSA solution (20 × 10^{-6} mol.kg^{-1}) at different temperatures is shown in Figs. 4 & 5. Similar trend is observed for other concentrations of plasma protein as obvious from data given in supplementary information.

Reported data showed that L_f values decrease with increasing concentration of pesticides and plasma protein in studied solutions. Decreasing L_f values showed the presence of strong molecular attractions among charged moieties of pesticides and plasma protein in solutions as a result distance among different molecules in solution decreases. Among the two pesticides, acephate develops stronger molecular association with plasma protein than dimethoate because in former case electronegativity difference among atoms in acephate molecules charged is greater hence possess comparatively stronger interactions [40]. With increasing temperature, second solvation layer of solute (pesticides) molecules rupture and water molecules releases into bulk, hence strong molecular attractions among pesticides and plasma protein molecules are present leading to decrease in L_f values with increasing temperature.

In the presence of ionic surfactants (CTAB and SDS), there develops a competition among hydrophilic head groups of surfactants and active binding sites of plasma protein to interact with pesticides molecules. Due to greater charge density on surfactant head groups than in plasma protein, pesticides tend to interact with surfactants more preferably [41]. As a result, L_f values decreases than in absence of surfactant molecules in solution. At post micellar concentration, where surfactants are present in micellar form and pesticides molecules get solvated in hydrophobic core of micelles and ion-hydrophobic and hydrophobic-hydrophobic interactions are present. While at micellar interface charge on ionic head groups is present as palisade layer/micellar layer and tend to develop ion-ion, ion-hydrophobic and ion-hydrophilic interactions with pesticides [42]. Therefore, in presence of micelles of ionic surfactants, binding of pesticides to plasma protein is lowered, as very less number of pesticides molecules become available to interact with plasma protein and resultantly gives toxic effects of pesticides on plasma protein (denaturation, decreased binding affinity with other bioactive molecules.) Among the two ionic surfactants, CTAB being a cationic surfactant, develops comparatively strong molecular interactions with negatively charged moieties in pesticide molecules whereas SDS being an anionic surfactant, possess repulsive interactions with pesticide molecules in solutions.

4. Conclusions

In present study, different volumetric and acoustic parameters were calculated using measured data of density and sound velocity at different temperature (293.15–313.15) K. Obtained results were interpreted in terms of organophosphate pesticides binding with plasma protein in aqueous and colloidal medium containing surfactants. Positively increasing values of apparent molar volume and decreasing values of L_f with increasing concentration of pesticides in solutions at each respective temperature indicated the existence of strong molecular

interactions among charged moieties in organophosphate pesticides and binding site II of human serum albumin. While in presence of ionic micelles, comparatively greater magnitude of V_ϕ values for pesticides-plasma protein solutions at respective temperatures showed that pesticides molecules get solvated in hydrophobic core of micelles with ion-hydrophobic and hydrophobic-hydrophobic binding forces. Similarly, at micellar interface, charge on ionic head groups is responsible to develop ion-ion, ion-hydrophobic and ion-hydrophilic interactions with pesticide molecules, representing biding of pesticide molecules with cell membrane. Positive values of Helper's constant indicated structure making behavior of both pesticides in aqueous plasma protein solutions.

In future, obtained results of this study may be helpful for the researchers working on binding of plasma protein with potential toxins. Effect of different parameters such as temperature and concentration of toxins on solvation shell structure of protein will also be investigated through the analysis of volumetric and acoustic parameters. More work is needed to be done under this topic using a very precise and cost effective thermo-acoustic approach.

CRediT authorship contribution statement

Iqra Arif: Conceptualization, Methodology. **Bushra Naseem:** Supervision, Data curation, Writing – original draft, Resources. **Ather Yaseen Khan:** Software, Validation. **Shahida Shujaat:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2023.122344.

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