Journal of chemical & engineering data

Article

Cite This: J. Chem. Eng. Data XXXX, XXX, XXX−XXX

pubs.acs.org/jced

Effect of Caffeine on the Physicochemical Properties of Neurotransmitter GABA: Thermodynamic and Theoretical Approach

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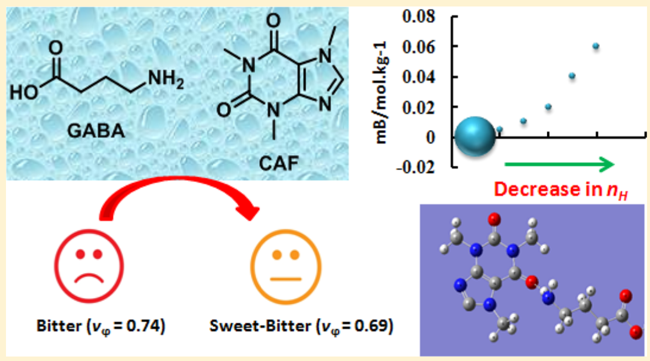
Supporting Information

ABSTRACT: The density, ρ, and the speed of sound, u, of γ-aminobutyric acid (GABA) in water and in (0.005, 0.01, 0.02, 0.04, and 0.06) mol·kg^{-1} aqueous caffeine (CAF) solutions were measured at temperatures, T = (293.15−318.15) K and P = 0.1 MPa. The measured data have been used to calculate apparent molar volumes at infinitesimal concentration ($V^{o}_{2,\phi}$), apparent molar isentropic compressibility ($K^{o}_{2,\phi}$), the corresponding transfer parameters, and other derived properties. The negative transfer values suggest the dominance of hydrophobic interactions and the structure-breaking tendency of CAF molecules. UV−visible spectroscopic studies have been carried out, and the shifts in the absorption spectra signify the role of hydrogen-bonding interactions. The structures of GABA and CAF have also been optimized in gas phase and solution phase by employing density functional theory at B3LYP/6-31+G* theoretical level, and the H-bond interactions between the two molecules have been studied. It is observed that there are strong H-bond interactions between GABA and CAF.



INTRODUCTION

γ-Aminobutyric acid (GABA) is a nonprotein amino acid present in a wide range of organisms.[1−3] It serves as a major inhibitory neurotransmitter in animals and also mediates signal transmission,[4] whereas in plants, it has been implicated in pH regulation, nitrogen storage, development, stress response,[1,3] and plant reproduction.[5] Studies show rapid and large accumulations of GABA in response to many diverse stimuli, such as heat shock, mechanical stimulation, hypoxia, drought, and cold.[1,3,6] The zwitterionic form of GABA diffuses as a spherical entity, whereas the conformational mobility allows it to bind to appropriate acceptors in its extended conformation and has implications for its biological activity.[7,8] Interaction of drugs with biomacromolecules in the receptor sites is an important phenomenon in physiological media, such as blood, membranes, and intra-/extracellular fluids. Xanthine-based drugs, such as caffeine (CAF), are the most widely consumed behaviorally active substance in the world. Almost all CAF comes from dietary sources (beverages and food), especially from coffee and tea. Acute and chronic CAF intake appear to have only minor negative consequences on health because of which the governmental regulatory agencies impose no restrictions on the use of CAF.[9−12] The mechanisms underlying the stimulant action of CAF on the central nervous system (CNS) are not yet understood. Chronic CAF use can cause tolerance in animals and humans, and subsequent abstinence from CAF can then lead to withdrawal syndromes.[11,12] The self-association of CAF molecules by hydrophobic interactions results in limited solubility in water, thus constraining their therapeutic applications.[13] The underlying mechanisms for GABA−CAF molecular interactions and their temperature dependence play an important role in understanding the drug action. However, very scarce literature data are available on the thermodynamic behavior of these amino acids; hence, a study on temperature effect will help to discuss solute hydration.[14] Therefore, it is imperative to study solute−cosolute interactions in aqueous media thermodynamically by monitoring different volumetric and ultrasonic properties, structurally as well as theoretically. These studies are vital in understanding molecular interactions (hydrophilic, hydrophobic, and ionic interactions) as they provide perceptible parameters for the elaboration of solute−solvent and solute−solute interactions in the solution phase.[15−17] The results have further been interpreted in terms of different molecular interactions in these aqueous ternary systems.

Received: April 16, 2019
Accepted: August 19, 2019

DOI: 10.1021/acs.jced.9b00327
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Table 1. Specifications of the Chemicals Used

				C, H, N, S analysis	
compound/(symbol)	source	CAS number	mass fraction purity[a]	calculated %	observed %
CAF	SRL	58-08-2	0.99	C (49.43)	C (49.54)
				N (28.84)	N (28.86)
				H (5.15)	H (5.18)
GABA	SRL	56-12-2	0.98	C (46.51)	C (46.59)
				N (13.49)	N (13.58)
				H (8.72)	H (8.80)

[a]Declared by the supplier.

Mathematical Expressions. The apparent molar volumes, $V_{2,\phi}$, have been determined using the ρ values as follows

$$V_{2,\phi} = \frac{M}{\rho} - \frac{(\rho - \rho_o)}{m_A \rho \rho_o} \quad (1)$$

where M is the molar mass, ρ is the density of the solution, and ρ_o is the density of the solvent (H_2O or H_2O + CAF).

The apparent molar volumes at infinitesimal concentration, $V^o_{2,\phi}$, have been evaluated for GABA by least-squares fitting of the following equation to the corresponding data as

$$V_{2,\phi} = V^o_{2,\phi} + S_v m_A \quad (2)$$

where S_v is the experimental slope that characterizes the pairwise interactions of the solute in solution phase.

The apparent molar volumes of transfer at infinitesimal concentration, $\Delta_{tr}V^o_{2,\phi}$, from water to aqueous CAF solutions have been determined as follows

$$\Delta_{tr}V^o_{2,\phi} = V^o_{2,\phi}(\text{in aqueous solutions of CAF}) - V^o_{2,\phi}(\text{in water}) \quad (3)$$

The apparent molar expansibilities $E^o_{2,\phi}$ ($E^o_{2,\phi} = (\partial V^o_{2,\phi}/\partial T)_P$) and the second derivative $(\partial^2 V^o_{2,\phi}/\partial T^2)_P$ have been obtained to study the effect of temperature on $V^o_{2,\phi}$, by fitting the following equation to the corresponding data

$$V^o_{2,\phi} = a + bT + cT^2 \quad (4)$$

where a, b, and c are constants, and T is the absolute temperature.

To have an insight into the qualitative information regarding the hydration of solute from thermal expansion, Hepler[18] used the following thermodynamic expression

$$\left(\frac{\partial C^o_{p,2}}{\partial p}\right)_T = -T\left(\frac{\partial^2 V^o_{2,\phi}}{\partial T^2}\right)_P \quad (5)$$

where $C^o_{p,2}$ is the partial molar heat capacity, and the sign of $(\partial C^o_{p,2}/\partial P)_T$ provides a direct probe of structure-making or breaking properties of stabilizers and destabilizers.

The taste quality of GABA can be judged by calculating the apparent massic volume, ν_ϕ, using the following relation

$$\nu_\phi = V^o_{2,\phi}/M \quad (6)$$

The apparent molar isentropic compressibility ($K_{s,2,\phi}$) values for GABA in water and in m_B = (0.005, 0.01, 0.02, 0.04 and 0.06) mol·kg^{-1} CAF solutions at T = (293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K were calculated using the following relation

$$K_{s,2,\phi} = (\kappa_s M/\rho) - \{(\kappa_s^o \rho - \kappa_s \rho_o)/(m \rho \rho_o)\} \quad (7)$$

where M is the molar mass and m_A is the molality of the solute. ρ, ρ^o and κ_s, κ_s^o are the densities and isentropic compressibilities of GABA in water or GABA in aqueous CAF solution and water or aqueous CAF, respectively.

The $K^o_{s,2}$ values have been calculated by least-squares fitting of the following equation to the corresponding $K_{s,2,\phi}$ data

$$K_{s,2,\phi} = K^o_{s,2} + S_K m \quad (8)$$

where S_K is the experimental slope. The $K^o_{s,2}$ values provide information about the solute–solvent interactions and can be expressed by the model reported by Millero et al.[19]

$$K^o_{s,2} = K^o_{s,2}(\text{int}) + K^o_{s,2}(\text{elect}) \quad (9)$$

The partial molar isentropic compressibilities of transfer ($\Delta_t K^o_{s,2}$) were calculated using the following equation

$$\Delta_t K^o_{s,2} = K^o_{s,2}\{\text{in CAF}_{(aq)}\} - K^o_{s,2}\{\text{in } H_2O\} \quad (10)$$

The hydration numbers (n_w) of GABA in water and in aqueous CAF solutions were calculated using the method reported by Millero et al.[19]

$$n_w = -K^o_{s,2}(\text{elect})/\kappa_s^o V_1^o \quad (11)$$

where κ_s^o and V_1^o are the compressibility and molar volume of bulk water/solvent, respectively.

■ EXPERIMENTAL SECTION

Materials. The chemicals GABA and CAF have been obtained from Sisco Research Laboratories (SRL), India, and were stored in a vacuum desiccator over $CaCl_2$ before use (Table 1). Both the chemicals used are of analytical grade and have mass fraction purity of 0.98 and 0.99, respectively. Solutions were prepared in Millipore, degassed water (specific conductance less than 1.29 × 10^{-6} Ω^{-1}·cm^{-1}) on mass basis by using a Mettler balance (model: AB265-S) having an accuracy of ±0.01 mg. The carbon and hydrogen percentages obtained from the C, H, N, S analysis suggests that the samples were pure and completely dried.

Techniques. The density ρ and the speed of sound u of solutions have been measured simultaneously by using a vibrating tube digital density meter and a sound velocity analyzer (Anton Paar, DSA 5000 M). The two-in-one instrument is equipped with both a density cell and a sound velocity cell, which are temperature-controlled by a built-in Peltier thermostat (PT-100) having an accuracy of ±0.01 K. The density meter was calibrated by Millipore degassed water at atmospheric pressure. The uncertainty in the measurement of density and speed of sound is 0.5 kg·m^{-3} and 2 m·s^{-1}, respectively.

DOI: 10.1021/acs.jced.9b00327
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Table 2. Densities (ρ) and Apparent Molar Volumes ($V_{2,\phi}$) of GABA in the Aqueous Solution of CAF at Temperatures T = (293.15−318.15) K and P = 0.1 MPa[a]

	m_B = 0.00 mol·kg^{-1}					
	T/K					
	293.15		298.15		303.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.00000	0.998207		0.997047		0.995649	
0.09972	1.000992	75.07(0.73)	0.999771	75.74(0.73)	0.998354	76.00(0.74)
0.14785	1.002314	75.12(0.73)	1.001048	75.90(0.74)	0.999634	76.08(0.74)
0.19424	1.003573	75.18((0.73)	1.002258	76.04(0.74)	1.000852	76.15(0.74)
0.24493	1.004936	75.23(0.73)	1.003556	76.20(0.74)	1.002165	76.24(0.74)
0.29367	1.006232	75.28(0.73)	1.004779	76.35(0.74)	1.003410	76.32(0.74)
0.34520	1.007584	75.34(0.73)	1.006039	76.53(0.74)	1.004711	76.39(0.74)
0.39278	1.008815	75.40(0.73)	1.007190	76.67(0.74)	1.005889	76.48(0.74)
	m_B = 0.00 mol·kg^{-1}					
	T/K					
	308.15		313.15		318.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.00000	0.994041		0.992215		0.990214	
0.09972	0.996682	76.73(0.74)	0.994848	76.91(0.75)	0.992851	76.96(0.75)
0.14785	0.997926	76.85(0.74)	0.996089	77.01(0.75)	0.994097	77.05(0.75)
0.19424	0.999104	76.97(0.75)	0.997262	77.14(0.75)	0.995285	77.12(0.75)
0.24493	1.000368	77.11(0.75)	0.998525	77.27(0.75)	0.996567	77.19(0.75)
0.29367	1.001564	77.23(0.75)	0.999722	77.38(0.75)	0.997781	77.27(0.75)
0.34520	1.002804	77.37(0.75)	1.000957	77.52(0.75)	0.999045	77.36(0.75)
0.39278	1.003924	77.50(0.75)	1.002075	77.66(0.75)	1.000200	77.43(0.75)
	m_B = 0.005 mol·kg^{-1}					
	T/K					
	293.15		298.15		303.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.00000	0.998731		0.997275		0.996169	
0.09880	1.001666	73.25(0.71)	1.000177	73.66(0.71)	0.999130	73.10(0.71)
0.14894	1.003121	73.38(0.71)	1.001576	74.04(0.72)	1.000594	73.25(0.71)
0.19827	1.004534	73.48(0.71)	1.002926	74.32(0.72)	1.002025	73.32(0.71)
0.24870	1.005955	73.60(0.71)	1.004248	74.69(0.72)	1.003456	73.45(0.71)
0.29968	1.007366	73.73(0.71)	1.005518	75.13(0.72)	1.004875	73.60(0.71)
0.34692	1.008656	73.83(0.72)	1.006698	75.38(0.73)	1.006184	73.69(0.71)
	m_B = 0.005 mol·kg^{-1}					
	T/K					
	308.15		313.15		318.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.00000	0.994279		0.992732		0.990833	
0.09880	0.997214	73.45(0.71)	0.995738	72.78(0.70)	0.993863	72.61(0.70)
0.14894	0.998630	73.84(0.72)	0.997235	72.87(0.71)	0.995372	72.70(0.70)
0.19827	1.000005	74.07(0.72)	0.998681	72.99(0.71)	0.996831	72.82(0.71)
0.24870	1.001351	74.42(0.72)	1.000144	73.09(0.71)	0.998301	72.94(0.71)
0.29968	1.002648	74.84(0.73)	1.001580	73.26(0.71)	0.999768	73.05(0.71)
0.34692	1.003860	75.05(0.73)	1.002909	73.36(0.71)	1.001122	73.11(0.71)
	m_B = 0.01 mol·kg^{-1}					
	T/K					
	293.15		298.15		303.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.00000	0.998986		0.997549		0.996422	
0.10046	1.001962	73.32(0.71)	1.000496	73.68(0.71)	0.999442	73.00(0.71)
0.14954	1.003368	73.54(0.71)	1.001871	74.01(0.72)	1.000879	73.15(0.71)
0.20038	1.004802	73.71(0.71)	1.003237	74.42(0.72)	1.002340	73.31(0.71)
0.24816	1.006117	73.90(0.72)	1.004459	74.87(0.73)	1.003681	73.49(0.71)
0.29756	1.007445	74.11(0.72)	1.005720	75.16(0.73)	1.005043	73.67(0.71)

DOI: 10.1021/acs.jced.9b00327
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Table 2. continued

m_B = 0.01 mol·kg^{-1}						
	T/K					
	293.15		298.15		303.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.34568	1.008698	74.35(0.72)	1.006829	75.69(0.73)	1.006328	73.89(0.72)
m_B = 0.01 mol·kg^{-1}						
	T/K					
	308.15		313.15		318.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.00000	0.994556		0.992974		0.990981	
0.10046	0.997555	73.28(0.71)	0.996053	72.54(0.70)	0.994083	72.39(0.70)
0.14954	0.998963	73.56(0.71)	0.997519	72.69(0.70)	0.995557	72.57(0.71)
0.20038	1.000366	73.94(0.72)	0.999010	72.86(0.71)	0.997062	72.71(0.70)
0.24816	1.001644	74.28(0.72)	1.000393	72.98(0.71)	0.998455	72.84(0.71)
0.29756	1.002917	74.65(0.72)	1.001791	73.15(0.71)	0.999863	73.01(0.71)
0.34568	1.004082	75.11(0.73)	1.003109	73.37(0.71)	1.001191	73.23(0.71)
m_B = 0.02 mol·kg^{-1}						
	T/K					
	293.15		298.15		303.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.00000	0.999492		0.998082		0.996912	
0.10103	1.002508	73.07(0.71)	1.001094	73.17(0.71)	0.999985	72.61(0.70)
0.19995	1.005359	73.37(0.71)	1.003864	73.86(0.71)	1.002888	72.93(0.71)
0.24876	1.006732	73.51(0.71)	1.005199	74.07(0.72)	1.004291	73.05(0.71)
0.29925	1.008127	73.65(0.71)	1.006521	74.38(0.72)	1.005717	73.19(0.71)
0.34811	1.009448	73.81(0.72)	1.007715	74.82(0.72)	1.007058	73.36(0.71)
0.39887	1.010782	74.00(0.72)	1.008969	75.10(0.73)	1.008422	73.56(0.71)
m_B = 0.02 mol·kg^{-1}						
	T/K					
	308.15		313.15		318.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.00000	0.995092		0.993452		0.991327	
0.10103	0.998168	72.66(0.70)	0.996587	72.13(0.70)	0.994480	72.04(0.70)
0.19995	1.001044	73.13(0.70)	0.999558	72.41(0.70)	0.997434	72.49(0.70)
0.24876	1.002406	73.40(0.71)	1.000995	72.53(0.70)	0.998849	72.70(0.70)
0.29925	1.003796	73.61(0.71)	1.002448	72.68(0.70)	1.000268	72.96(0.71)
0.34811	1.005075	73.93(0.71)	1.003843	72.79(0.71)	1.001647	73.10(0.71)
0.39887	1.006388	74.19(0.72)	1.005246	72.97(0.71)	1.003021	73.32(0.71)
m_B = 0.04 mol·kg^{-1}						
	T/K					
	293.15		298.15		303.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.00000	1.000685		0.999091		0.997986	
0.09755	1.003625	72.73(0.70)	1.002021	72.90(0.71)	1.001001	72.08(0.70)
0.20503	1.006791	72.87(0.70)	1.005030	73.76(0.72)	1.004211	72.39(0.70)
0.29503	1.009380	72.98(0.71)	1.007377	74.46(0.72)	1.006799	72.69(0.71)
0.34488	1.010793	73.04(0.71)	1.008619	74.82(0.72)	1.008206	72.83(0.71)
0.37637	1.011679	73.08(0.71)	1.009426	74.93(0.73)	1.009102	72.86(0.71)
0.44210	1.013502	73.16(0.71)	1.011006	75.31(0.73)	1.010886	73.09(0.71)
m_B = 0.04 mol·kg^{-1}						
	T/K					
	308.15		313.15		318.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.00000	0.996095		0.994510		0.992156	
0.09755	0.999108	72.17(0.70)	0.997596	71.48(0.69)	0.995265	71.33(0.69)
0.20503	1.002269	72.72(0.70)	1.000894	71.75(0.70)	0.998500	72.04(0.70)

DOI: 10.1021/acs.jced.9b00327
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Table 2. continued

	m_B = 0.04 mol·kg^{-1}					
	T/K					
	308.15		313.15		318.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.29503	1.004748	73.33(0.71)	1.003555	72.04(0.70)	1.001024	72.75(0.70)
0.34488	1.006079	73.61(0.71)	1.005001	72.17(0.70)	1.002378	73.07(0.70)
0.37637	1.006932	73.70(0.72)	1.005921	72.20(0.70)	1.003223	73.25(0.70)
0.44210	1.008587	74.12(0.72)	1.007781	72.37(0.70)	1.004935	73.62(0.71)
	m_B = 0.06 mol·kg^{-1}					
	T/K					
	293.15		298.15		303.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.00000	1.001781		1.000023		0.999147	
0.10629	1.004926	73.22(0.71)	1.003215	72.86(0.71)	1.002443	71.90(0.70)
0.20687	1.007841	73.30(0.71)	1.006037	73.61(0.71)	1.005484	72.07(0.70)
0.30975	1.010765	73.38(0.72)	1.008697	74.47(0.72)	1.008509	72.26(0.70)
0.35514	1.012034	73.42(0.72)	1.009810	74.83(0.72)	1.009803	72.38(0.70)
0.38764	1.012935	73.45(0.73)	1.010623	74.98(0.73)	1.010742	72.41(0.70)
0.44993	1.014643	73.51(0.73)	1.012094	75.38(0.73)	1.012480	72.56(0.70)
	m_B = 0.06 mol·kg^{-1}					
	T/K					
	308.15		313.15		318.15	
m_A/(mol·kg^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})	$\rho \times 10^{-3}$/(kg·m^{-3})	$V_{2,\phi} \times 10^6$/(m^3·mol^{-1})
0.00000	0.997015		0.995632		0.992958	
0.10629	1.000308	72.03(0.70)	0.999034	71.04(0.69)	0.996348	71.26(0.69)
0.20687	1.003191	72.95(0.71)	1.002169	71.23(0.69)	0.999397	71.82(0.69)
0.30975	1.005938	73.79(0.71)	1.005303	71.38(0.69)	1.002367	72.36(0.70)
0.35514	1.007082	74.16(0.72)	1.006653	71.47(0.69)	1.003596	72.69(0.70
0.38764	1.007946	74.25(0.72)	1.007613	71.53(0.69)	1.004508	72.79(0.70)
0.44993	1.009442	74.71(0.72)	1.009425	71.65(0.69)	1.006123	73.20(0.71)

[a]The standard uncertainty: $u(\rho)$ = 0.5 kg·m^{-3}; $u(V_{2,\phi})$ = (0.51−0.25) × 10^{-6} m^3 ·mol^{-1} for the low ($m_A \leq 0.10$ mol·kg^{-1}) and high ($m_A \leq 0.45$ mol·kg^{-1}) molality ranges; $u(m)$ = 0.01 mol·kg^{-1}; $u(T)$ = 0.01 K, $u(P)$ = 0.5 kPa (level of confidence is 0.68). Apparent massic volumes (ν_ϕ) are given in parenthesis.

The UV−visible absorption spectra for aqueous CAF (pure) as well as in the presence of GABA have been recorded on a Shimadzu (UV-1800) spectrophotometer equipped with (1.0 cm in width) quartz cells. The reproducibility for λ_{max} of the spectra was within ±0.1 nm.

Density functional theory (DFT)[20] calculations have been performed using Gaussian 09W package, the windows version of the Gaussian 09 suite of programs.[21] Complete optimizations were carried out on GABA and CAF using the B3LYP/6-31+G* basis set without any symmetry constraints. Frequencies were computed for the optimized structures to characterize each stationary point as a minimum or a transition state and to determine ZPVE (zero-point vibrational energy) values. Solvent effect has been studied using SCRF (self-consistent reaction field) (SCI PCM, solvent = water, i.e., self-consistent isodensity-polarized continuum model) calculations at B3LYP/6-31+G* level.

■ RESULTS AND DISCUSSION

Apparent Molar Volumes. The densities, ρ, of GABA in water and in aqueous solutions of CAF at m_B (molality of CAF in water) = 0.005, 0.01, 0.02, 0.04, and 0.06 mol·kg^{-1} have been measured at temperatures of 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K and at p = 0.1 MPa. The ρ values for GABA increase with the molality of the solute, m_A, as well as with the molality of CAF, m_B, but decrease with temperature. The densities of CAF in the water system have been compared with the literature data at temperatures T = 298.15, 303.15, and 313.15 K (Figure S1a−c). The density values reported in the present work are in good agreement with the values reported by Jahagirdhar et al.[22] At 303.15 and 313.15 K, the present values are slightly higher than the reported values.

Similarly, literature comparison was done for the density values for GABA in the water system (Figure S2). At 293.15 K (Figure S2a), the values of density reported by Romero and Cadena[23] vary to a large extent from the present values. This is because the molality range taken by Romero and Cadena[23] is very less, that is, from m_A = 0.002 to 0.0168 mol·kg^{-1}, whereas the present work reports the values of molality range of m_A = 0.099−0.393 mol·kg^{-1}. Similar is the case observed at T = 303.15 K (Figure S2c). At 298.15 K (Figure S2b), the densities in the present work agree well with the literature data reported by Banipal et al.[24] and Hakin and Liu,[25] except in case of the data reported by Hakin and Liu[25] where large deviations have been observed. In this case also, the molality range varies to a large extent. At 308.15 K (Figure S2d), the density values deviate from the values reported by Banipal et al.[24] at higher molalities, and also Romero and Cadena[23] report the values at lower molalities. That is why large deviations are observed. At

DOI: 10.1021/acs.jced.9b00327
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Table 3. Infinite Dilution Standard Partial Molar Volumes, $V^{\circ}_{2,\phi}$, of GABA in Aqueous CAF Solutions at T = (293.15−318.15) K and P = 0.1 MPa

	$V^{\circ}_{2,\phi} \times 10^6/(\mathrm{m^3 \cdot mol^{-1}})$					
	T/K					
[a] $m_B/(\mathrm{mol \cdot kg^{-1}})$	293.15	298.15	303.15	308.15	313.15	318.15
0.0	74.95[b] (1.11), 74.98[f]	75.42 (3.17), 75.51[c,d,g,h,i,j], 76.35[e], 75.64[f], 75.50[j]	75.83 (1.64), 75.89[f]	76.46 (2.63). 76.59[c], 76.61[e]	76.64 (2.56)	76.81 (1.57), 76.80[c], 76.82[e]
0.005	73.02 (2.34)	72.96 (7.02)	72.87 (2.35)	72.82 (6.52)	72.52 (2.39)	72.40 (2.07)
0.01	72.90 (4.09)	72.81 (8.14)	72.60 (3.64)	72.48 (7.40)	72.19 (3.27)	72.05 (3.28)
0.02	72.75 (3.07)	72.51 (6.45)	72.29 (3.10)	72.11 (5.15)	71.85 (2.77)	71.62 (4.30)
0.04	72.61 (1.24)	72.28 (7.08)	71.80 (2.90)	71.60 (5.68)	71.22 (2.64)	70.68 (6.78)
0.06	73.13 (0.81)	72.08 (7.49)	71.68 (1.90)	71.28 (7.82)	70.85 (1.75)	70.65 (5.61)

[a] m_B is the molality of CAF in water. [b] S_v ($\mathrm{m^3 \cdot kg \cdot mol^{-2}}$) is the slope. Standard deviations lie in the range of ± (0.01−0.05) × 10^6 $\mathrm{m^3 \cdot mol^{-1}}$. [c] Ref 27. [d] Ref 28. [e] Ref 29. [f] Ref 30. [g] Ref 31. [h] Ref 32. [i] Ref 33. [j] Ref 34. [k] Ref 35.

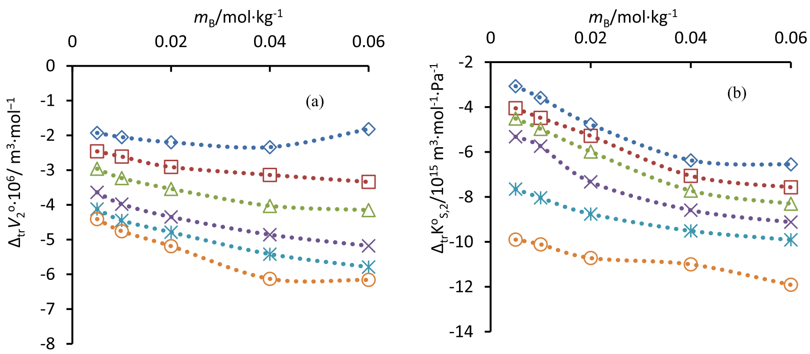

Figure 1. (a) Partial molar volumes of transfer, $\Delta_{tr}V^{\circ}_2$, and (b) partial molar isentropic compressibility of transfer, $\Delta_{tr}K^{\circ}_{s,2}$, for GABA vs molalities, m_B, of CAF at temperatures: blue diamond◊, 293.15 K; red square, 298.15 K; green triangle up open, 303.15 K; violet multiplication, 308.15 K; sky blue asterisk, 313.15 K; orange circle, 318.15 K.

Table 4. Partial Molar Expansion Coefficients, $(\partial V^{\circ}_{2,\phi}/\partial T)_P$, and Second-Order Derivatives, $(\partial^2 V^{\circ}_{2,\phi}/\partial T^2)_P$, of GABA in CAF at T = (293.15−318.15) K and P = 0.1 MPa

	$10^6 \cdot (\partial V^{\circ}_{2,\phi}/\partial T)_P/(\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}})$							
	T/K							
[a] $m_B/(\mathrm{mol \cdot kg^{-1}})$	293.15	298.15	303.15	308.15	313.15	318.15	[b] SD	$10^6 \cdot (\partial^2 V^{\circ}_{2,\phi}/\partial T^2)_P/(\mathrm{m^3 \cdot mol^{-1} \cdot K^{-2}})$
0.00	0.121	0.103	0.086	0.069	0.051	0.034	0.108	−0.00346
0.005	−0.005	−0.013	−0.021	−0.030	−0.038	−0.046	0.056	−0.00163
0.01	−0.025	−0.029	−0.034	−0.038	−0.042	−0.046	0.047	−0.00081
0.02	−0.043	−0.043	−0.044	−0.045	−0.046	−0.047	0.021	−0.00016
0.04	−0.063	−0.067	−0.072	−0.077	−0.081	−0.086	0.091	−0.00093
0.06	−0.168	−0.138	−0.109	−0.079	−0.050	−0.020	0.137	0.00590

[a] m_B is the molality of CAF in water. [b] SD is the standard deviation in partial molar expansion coefficients $(\partial V^{\circ}_{2,\phi}/\partial T)_P$.

313.15 K (Figure S2f) and 318.15 K (Figure S2e), the present values of density are in good agreement with the values reported by Rajagopal and Jayabalakrishnan[26] and that at lower molalities reported by Banipal et al.[24] At higher molalities, the density values reported by Banipal et al.[24] are more compared with the present data. The ρ and $V_{2,\phi}$ values for GABA in water and in aqueous CAF solutions as a function of m_A, m_B, and T are given in Table 2. The $V_{2,\phi}$ values for GABA increase with solute molality, but the magnitude is comparatively less in aqueous CAF solutions as compared to that in water.

The $V^{\circ}_{2,\phi}$ values for GABA in water (Table 3) agree well with the literature values.[27−35] The S_v values are found to be positive for GABA in water as well as in aqueous solutions of CAF. In water, the $V^{\circ}_{2,\phi}$ values for GABA shows a slight increase with temperature, and this behavior is characteristic of solutes showing hydrophilic hydration.[30] However, in the presence of CAF, the $V^{\circ}_{2,\phi}$ values decrease with temperature as well as with m_B.

The $\Delta_{tr}V^{\circ}_{2,\phi}$ values (Figure 1) were found to be negative when GABA was transferred from water to aqueous CAF solutions. According to the cosphere overlap model developed by Gurney,[36] the various possible types of interactions in the GABA−$CAF_{(aq)}$ system are as follows: (i) hydrophilic−hydrophilic interactions among the polar groups of GABA

DOI: 10.1021/acs.jced.9b00327
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Table 5. Speed of Sound (u), Apparent Molar Isentropic Compressibilities ($K_{s,2,\phi}$), and Acoustic Impedance (Z) of GABA in Water and in CAF Solutions at T = (293.15−318.15) K and P = 0.1 MPa[c]

	[b]m_B = 0.00 mol·kg^{-1}					
	T/K					
	293.15			298.15		
[a]m_A/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^{2}s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})
0.00000	1482.94			1496.92		
0.09972	1491.39	−30.59	1.493	1504.99	−26.84	1.505
0.14785	1495.44	−30.31	1.499	1508.89	−26.62	1.510
0.19424	1499.34	−30.08	1.505	1512.65	−26.43	1.516
0.24493	1503.55	−29.75	1.511	1516.75	−26.19	1.522
0.29367	1507.61	−29.52	1.517	1520.69	−25.96	1.528
0.34520	1511.84	−29.18	1.523	1524.85	−25.69	1.534
0.39278	1515.73	−28.89	1.529	1528.65	−25.42	1.540
	[b]m_B = 0.00 mol·kg^{-1}					
	T/K					
	303.15			308.15		
[a]m_A/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})
0.00000	1509.25			1519.88		
0.09972	1517.04	−24.32	1.515	1527.44	−21.91	1.522
0.14785	1520.80	−24.18	1.520	1531.09	−21.75	1.528
0.19424	1524.41	−24.00	1.526	1534.59	−21.53	1.533
0.24493	1528.37	−23.85	1.532	1538.45	−21.40	1.539
0.29367	1532.17	−23.70	1.537	1542.11	−21.16	1.545
0.34520	1536.18	−23.53	1.543	1546.00	−20.96	1.550
0.39278	1539.87	−23.35	1.549	1549.57	−20.75	1.556
	[b]m_B = 0.00 mol·kg^{-1}					
	T/K					
	313.15			318.15		
[a]m_A/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})
0.00000	1528.94			1536.53		
0.09972	1536.28	−20.21	1.528	1543.67	−18.85	1.533
0.14785	1539.81	−20.01	1.534	1547.11	−18.70	1.538
0.19424	1543.22	−19.84	1.539	1550.42	−18.56	1.543
0.24493	1546.95	−19.68	1.545	1554.03	−18.42	1.549
0.29367	1550.53	−19.53	1.550	1557.48	−18.24	1.554
0.34520	1554.32	−19.35	1.556	1561.12	−18.05	1.560
0.39278	1557.81	−19.17	1.561	1564.46	−17.88	1.565
	[b]m_B = 0.005 mol·kg^{-1}					
	T/K					
	293.15			298.15		
[a]m_A/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})
0.00000	1483.00			1497.15		
0.09880	1491.31	−31.91	1.494	1504.82	−28.68	1.505
0.14894	1495.09	−29.90	1.500	1508.50	−27.43	1.511
0.19827	1498.93	−29.18	1.506	1511.93	−26.12	1.517
0.24870	1502.49	−27.79	1.511	1515.26	−24.69	1.523
0.29968	1505.74	−26.11	1.517	1518.22	−22.76	1.528
0.34692	1508.96	−25.31	1.522	1521.47	−22.35	1.533
	[b]m_B = 0.005 mol·kg^{-1}					
	T/K					
	303.15			308.15		
[a]m_A/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})
0.00000	1509.48			1520.09		
0.09880	1516.71	−23.46	1.515	1527.54	−25.69	1.523
0.14894	1520.35	−23.13	1.521	1531.06	−24.28	1.529
0.19827	1523.86	−22.76	1.527	1534.54	−23.55	1.535
0.24870	1527.44	−22.39	1.533	1537.94	−22.56	1.541

DOI: 10.1021/acs.jced.9b00327
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Table 5. continued

	$^{b}m_B$ = 0.005 mol·kg^{-1}, T/K					
	303.15			308.15		
$^{a}m_A$/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})
0.29968	1531.04	−22.02	1.538	1541.07	−21.15	1.546
0.34692	1534.35	−21.74	1.544	1544.10	−20.46	1.551

	$^{b}m_B$ = 0.005 mol·kg^{-1}, T/K					
	313.15			318.15		
$^{a}m_A$/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})
0.00000	1529.13			1536.69		
0.09880	1537.18	−27.00	1.530	1544.98	−27.61	1.535
0.14894	1541.15	−26.41	1.537	1548.96	−26.56	1.541
0.19827	1545.01	−25.88	1.543	1552.87	−25.95	1.547
0.24870	1548.91	−25.39	1.549	1556.77	−25.30	1.553
0.29968	1552.68	−24.64	1.555	1560.34	−24.12	1.559
0.34692	1556.15	−24.09	1.560	1563.85	−23.66	1.565

	$^{b}m_B$ = 0.01 mol·kg^{-1}, T/K					
	293.15			298.15		
$^{a}m_A$/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})
0.00000	1483.47			1497.57		
0.10046	1492.18	−33.60	1.495	1505.66	−30.32	1.507
0.14954	1496.36	−32.99	1.502	1509.55	−29.67	1.513
0.20038	1500.65	−32.45	1.508	1513.55	−29.01	1.519
0.24816	1504.67	−31.95	1.514	1517.31	−28.39	1.525
0.29756	1508.74	−31.36	1.520	1521.00	−27.56	1.531
0.34568	1512.64	−30.71	1.526	1524.66	−26.80	1.536

	$^{b}m_B$ = 0.01 mol·kg^{-1}, T/K					
	303.15			308.15		
$^{a}m_A$/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})
0.00000	1509.85			1520.43		
0.10046	1518.13	−28.86	1.517	1528.21	−26.72	1.525
0.14954	1522.12	−28.40	1.523	1531.91	−25.99	1.531
0.20038	1526.27	−28.09	1.530	1535.78	−25.47	1.537
0.24816	1530.15	−27.77	1.536	1539.34	−24.86	1.542
0.29756	1534.12	−27.37	1.542	1542.93	−24.14	1.548
0.34568	1537.92	−26.89	1.547	1546.38	−23.39	1.553

	$^{b}m_B$ = 0.01 mol·kg^{-1}, T/K					
	313.15			318.15		
$^{a}m_A$/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})
0.00000	1529.43			1536.97		
0.10046	1537.75	−27.76	1.531	1545.50	−28.49	1.536
0.14954	1541.75	−27.32	1.538	1549.63	−28.08	1.542
0.20038	1545.91	−26.98	1.544	1553.90	−27.75	1.549
0.24816	1549.76	−26.61	1.550	1557.86	−27.38	1.555
0.29756	1553.71	−26.20	1.556	1561.86	−26.86	1.561
0.34568	1557.51	−25.74	1.562	1565.88	−26.57	1.567

	$^{b}m_B$ = 0.02 mol·kg^{-1}, T/K					
	293.15			298.15		
$^{a}m_A$/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi}$ × 10^{15}/(m^3·mol^{-1}·Pa^{-1})	Z × 10^6/(kg·m^2.s^{-1})
0.00000	1483.98			1498.04		
0.10103	1492.79	−33.95	1.497	1505.83	−28.25	1.508

DOI: 10.1021/acs.jced.9b00327
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Table 5. continued

	$^b m_B$ = 0.02 mol·kg^{-1}					
	T/K					
	293.15			298.15		
$^a m_A$/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2.s^{-1})
0.19995	1500.72	−31.35	1.509	1511.77	−22.48	1.518
0.24876	1504.41	−30.17	1.515	1514.23	−20.14	1.523
0.29925	1508.19	−29.20	1.521	1516.42	−17.67	1.527
0.34811	1511.66	−28.14	1.526	1518.66	−15.96	1.531
0.39887	1515.34	−27.34	1.532	1520.22	−13.57	1.535
	$^b m_B$ = 0.02 mol·kg^{-1}					
	T/K					
	303.15			308.15		
$^a m_A$/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2.s^{-1})
0.00000	1510.28			1520.80		
0.10103	1518.61	−29.02	1.518	1529.06	−28.86	1.526
0.19995	1526.36	−27.37	1.531	1537.06	−28.01	1.539
0.24876	1529.89	−26.29	1.536	1540.76	−27.07	1.545
0.29925	1533.56	−25.49	1.542	1544.95	−27.05	1.551
0.34811	1537.03	−24.71	1.548	1549.07	−26.97	1.557
0.39887	1540.71	−24.16	1.553	1552.78	−26.08	1.563
	$^b m_B$ = 0.02 mol·kg^{-1}					
	T/K					
	313.15			318.15		
$^a m_A$/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2·s^{-1})
0.00000	1529.75			1537.24		
0.10103	1538.14	−28.02	1.533	1545.73	−28.84	1.537
0.19995	1546.05	−26.73	1.545	1553.78	−27.49	1.549
0.24876	1549.76	−25.95	1.551	1557.69	−26.93	1.555
0.29925	1553.62	−25.36	1.557	1561.78	−26.52	1.562
0.34811	1557.22	−24.71	1.562	1565.49	−25.86	1.567
0.39887	1561.01	−24.20	1.568	1569.43	−25.33	1.574
	$^b m_B$ = 0.04 mol·kg^{-1}					
	T/K					
	293.15			298.15		
$^a m_A$/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2·s^{-1})
0.00000	1485.11			1499.04		
0.09755	1494.01	−35.95	1.499	1507.06	−31.90	1.510
0.20503	1503.49	−34.54	1.514	1515.60	−30.01	1.524
0.29503	1510.95	−32.96	1.525	1522.24	−27.97	1.535
0.34488	1515.02	−32.29	1.531	1525.71	−26.82	1.540
0.37637	1517.57	−31.91	1.535	1527.66	−25.94	1.543
0.44210	1522.47	−30.66	1.543	1531.57	−24.09	1.550
	$^b m_B$ = 0.04 mol·kg^{-1}					
	T/K					
	303.15			308.15		
$^a m_A$/(mol·kg^{-1})	u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2·s^{-1})	u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2·s^{-1})
0.00000	1511.15			1521.58		
0.09755	1519.41	−30.50	1.521	1529.46	−28.82	1.528
0.20503	1528.11	−28.87	1.534	1537.43	−26.17	1.541
0.29503	1535.05	−27.45	1.545	1543.76	−24.32	1.551
0.34488	1538.70	−26.61	1.551	1547.17	−23.46	1.557
0.37637	1540.79	−25.89	1.554	1549.07	−22.69	1.560
0.44210	1545.03	−24.41	1.561	1552.81	−20.94	1.567

DOI: 10.1021/acs.jced.9b00327
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Table 5. continued

$^{a}m_A$/(mol·kg^{-1})	$^{b}m_B$ = 0.04 mol·kg^{-1}, T/K = 313.15: u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2·s^{-1})	T/K = 318.15: u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2.s^{-1})
0.00000	1530.43			1537.84		
0.09755	1538.53	−28.26	1.535	1545.69	−28.23	1.538
0.20503	1547.16	−27.01	1.548	1554.06	−26.68	1.552
0.29503	1553.86	−25.39	1.559	1560.56	−24.77	1.562
0.34488	1557.49	−24.67	1.564	1564.16	−24.05	1.568
0.37637	1559.53	−23.98	1.568	1566.35	−23.55	1.571
0.44210	1563.85	−22.80	1.575	1570.30	−21.90	1.578

$^{a}m_A$/(mol·kg^{-1})	$^{b}m_B$ = 0.06 mol·kg^{-1}, T/K = 293.15: u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2·s^{-1})	T/K = 298.15: u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2.s^{-1})
0.00000	1486.22			1500.06		
0.10629	1496.04	−36.07	1.503	1509.03	−33.27	1.514
0.20687	1504.82	−34.23	1.517	1517.36	−31.89	1.527
0.30975	1513.47	−32.76	1.530	1525.76	−30.52	1.540
0.35514	1517.04	−31.92	1.535	1529.25	−29.66	1.546
0.38764	1519.76	−31.65	1.539	1531.83	−29.32	1.550
0.44993	1524.27	−30.34	1.547	1536.37	−28.15	1.557

$^{a}m_A$/(mol·kg^{-1})	$^{b}m_B$ = 0.06 mol·kg^{-1}, T/K = 303.15: u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2·s^{-1})	T/K = 308.15: u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2·s^{-1})
0.00000	1512.10			1522.43		
0.10629	1521.53	−32.04	1.525	1531.15	−30.14	1.532
0.20687	1530.33	−31.31	1.538	1539.15	−28.45	1.544
0.30975	1539.17	−30.49	1.552	1547.45	−27.51	1.557
0.35514	1542.99	−30.04	1.557	1550.81	−26.64	1.563
0.38764	1545.72	−29.81	1.561	1553.32	−26.37	1.566
0.44993	1550.88	−29.25	1.569	1557.92	−25.44	1.574

$^{a}m_A$/(mol·kg^{-1})	$^{b}m_B$ = 0.06 mol·kg^{-1}, T/K = 313.15: u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2.s^{-1})	T/K = 318.15: u/(m·s^{-1})	$K_{S,2,\phi} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})	$Z \times 10^6$/(kg·m^2.s^{-1})
0.00000	1531.20			1538.52		
0.10629	1540.40	−29.49	1.538	1547.42	−29.92	1.542
0.20687	1548.93	−28.65	1.551	1555.62	−28.65	1.555
0.30975	1557.47	−27.81	1.564	1564.00	−27.76	1.568
0.35514	1561.16	−27.40	1.570	1567.56	−27.13	1.573
0.38764	1563.80	−27.15	1.574	1570.10	−26.82	1.577
0.44993	1568.65	−26.46	1.582	1574.80	−25.93	1.584

[a] m_A is the molality of GABA in water. [b] m_B is the molality of CAF in water. [c] The standard uncertainty: $u(u)$ = 2 m·s^{-1}; $u(K_{s,2,\phi})$ = 0.48 × 10^{-15} m^3·mol^{-1}·Pa^{-1} for the low ($m_A \leq$ 0.10 mol·kg^{-1}) and 0.31 × 10^{-15} m^3·mol^{-1}·Pa^{-1} for the high ($m_A \leq$ 0.45 mol·kg^{-1}) molality ranges; $u(m)$ = 0.01 mol·kg^{-1}; $u(T)$ = 0.01 K; $u(P)$ = 0.5 kPa (level of confidence is 0.68).

and CAF; (ii) hydrophobic−hydrophilic interactions between the nonpolar and polar parts of GABA and CAF, respectively, and vice versa; and (iii) hydrophobic−hydrophobic interactions among the nonpolar parts of GABA and CAF. The overlap of hydrophobic/hydrophilic−hydrophilic/hydrophobic cospheres results in the observed negative $\Delta_{tr}V^{o}_{2,\phi}$ values, suggesting the dominance of type (ii) and type (iii) interactions over type (i) interactions. Further, the magnitude of transfer increases with temperature. As the molecules of GABA and CAF are embedded with both the hydrophilic and hydrophobic groups, the resultant overlap is concentration- and temperature-dependent.

$E^{o}_{2,\phi}$ values (Table 4) are positive for GABA in water but negative in aqueous CAF solutions. Therefore, from the data in Table 4, it may be inferred that the negative $\partial^2 V^{o}_{2,\phi}/\partial T^2$ values for GABA in water as well as in aqueous CAF solutions show structure-breaking behavior, whereas at m_B = 0.06 mol·kg^{-1}, the positive $\partial^2 V^{o}_{2,\phi}/\partial T^2$ values indicated structure-making behavior. The addition of a cosolute to the aqueous solution of a solute may either enhance or reduce the solubility of the

DOI: 10.1021/acs.jced.9b00327
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Table 6. Partial Molar Isentropic Compressibilities ($K^{o}_{s,2}$) at Infinite Dilution of GABA in Water and in CAF Solutions at T = (293.15−318.15) K and P = 0.1 MPa

	$K^{o}_{s,2} \times 10^{15}$/(m^3·mol^{-1}·Pa^{-1})					
	T/K					
[a]m_B/(mol·kg^{-1})	293.15	298.15	303.15	308.15	313.15	318.15
0.0	−31.17	−27.34, −27.10[b,c], −29.95[d,e,f]	−24.65	−22.32	−20.53	−19.19
0.005	−34.24	−31.39	−24.16	−27.64	−28.18	−29.09
0.01	−34.76	−31.82	−29.62	−28.06	−28.57	−29.30
0.02	−35.94	−32.62	−30.63	−29.65	−29.29	−29.91
0.04	−37.54	−34.40	−32.37	−30.91	−30.04	−30.19
0.06	−37.72	−34.91	−32.95	−31.44	−30.44	−31.10

[a]Standard deviation lies in the range of ± (0.008−0.06) × 10^{-15} m^3·mol^{-1}·Pa^{-1}. [b]Ref 32. [c]Ref 34. [d]Ref 31. [e]Ref 33. [f]Ref 38.

solute in water depending upon the nature and size of the cosolute. The observed negative $\Delta_{tr}V^{o}_{2,\phi}$ values for some of these solutes over a certain concentration range of CAF show the salting-out effect.

Apparent Massic Volume and Taste Quality. The taste quality in relation to ν_ϕ values (Table 2) follows the order: salty < sour < sweet < bitter.[37] The ν_ϕ values for GABA in water fall in the bitter range (0.71−0.93) cm^3 g^{-1}, and the values increase with a rise in temperature, whereas in aqueous CAF solutions, the values shift from the bitter to sweet-bitter taste range with an increasing molality of the cosolute. Moreover, the effect of temperature is also reversed in the presence of CAF, and hence at higher temperatures, the ternary solution of GABA in aqueous CAF shows the sweet-bitter taste behavior.

Apparent Molar Isentropic Compressibility ($K_{s,2,\phi}$). The isentropic compressibilities (κ_s) were calculated from the measured speed of sound (u) (Table 5) and density data (Table 2) using the relation: $\kappa_s = 1/u^2\rho$. The speed of sound values for GABA in aqueous solutions of CAF increase with an increase in the molality of the solute, cosolute, and temperature. The speed of sound of CAF in the water system has been compared with the literature data at temperatures T = 298.15, 303.15, and 313.15 K (Figure S3a−c). The values of u reported in the present study are lesser than the values reported by Jahagirdhar et al.[22] at all the studied temperatures. On similar lines, the literature comparison was done for the u values of GABA in the water system at T = 308.15, 313.15, and 318.15 K (Figure S4a−c). The present values of u agree well with the values reported by Rajagopal and Jayabalakrishnan[26] at lower molality at 308.15 K (Figure S4a), whereas the values reported at higher temperatures (Figure S4b,c) are slightly higher than the literature values reported by Rajagopal and Jayabalakrishnan.[26]

The $K_{s,2,\phi}$ values are negative and their magnitudes decrease with an increase in the temperature and concentration of both solute and cosolute (Table 5). The uncertainty in the $K_{s,2,\phi}$ values arising from the measurements of various quantities such as density, molality, and temperature ranges from (0.27 to 0.11) × 10^{-15} m^3·mol^{-1}·Pa^{-1} for the low ($m_A \leq 0.09$ mol·kg^{-1}) and higher concentration ranges. At infinitesimal concentration, the apparent molar isentropic compressibility ($K_{s,2,\phi}$) becomes equal to the partial molar isentropic compressibility ($K^{o}_{s,2}$). The $K^{o}_{s,2}$ values for GABA in water agree well (Table 6) with the reported values.[31−34,38]

Millero et al.[19] further made an approximation to the intrinsic partial molar isentropic compressibility as: $K^{o}_{s,2}$ (int) ≈ 0, as one would expect $K^{o}_{s,2}$ (int) to be very small. Therefore, $K^{o}_{s,2}$ may be thought to represent the electrostriction partial molar isentropic compressibility, $K^{o}_{s,2}$ (elect). The $K^{o}_{s,2}$ values of GABA are negative in water as well as in the aqueous solutions of CAF, which may be because of the hydration of the solutes, as the hydrated water molecules are already compressed and thus less compressible than that present in the bulk. The magnitude of $K^{o}_{s,2}$ values decreases with temperature but increases with the concentration of CAF.

The $\Delta_t K^{o}_{s,2}$ values are negative and their magnitudes increase with the temperature and concentration of CAF (Figure 1). This suggests the predominance of hydrophobic−ionic interactions over the hydrophilic−ionic interactions and strengthening of these interactions over the entire range of concentration studied. Because of the interactions among the hydrophobic sites of the GABA and CAF molecules, the hydration spheres of the charged centers get disrupted. These results are in agreement with the volumetric study results.

$K^{o}_{s,2}$ (elect) is considered approximately equal to $K^{o}_{s,2}$ (GABA), as $K^{o}_{s,2}$ (int) ≈ 0. The magnitude of n_w values (Table 7) decreases drastically in aqueous CAF solutions as compared to that in water and also decreases with the rise of temperature. The decrease in the hydration number of GABA because of the presence of CAF is attributed to the removal of water molecules from the hydration sphere because of the overlap of the cospheres of CAF and GABA molecules. As the temperature is increased, some water molecules from the hydration cosphere relax to the bulk because of thermal agitation, thereby decreasing the hydration number. This shows that CAF has a dehydrating effect on GABA.

Table 7. Hydration Numbers (n_W) of GABA in Water and in CAF Solutions at T = (293.15−318.15) K and P = 0.1 MPa

	n_W					
	T/K					
[a]m_B/(mol·kg^{-1})	293.15	298.15	303.15	308.15	313.15	318.15
0.0	3.794	3.383	3.092	2.830	2.625	2.468
0.005	0.071	0.066	0.052	0.060	0.062	0.064
0.01	0.072	0.067	0.064	0.061	0.062	0.064
0.02	0.075	0.069	0.066	0.064	0.064	0.066
0.04	0.079	0.073	0.070	0.067	0.066	0.067
0.06	0.079	0.073	0.070	0.067	0.066	0.067

[a]m_B is the molality of CAF in water.

Apparent Massic Isentropic Compressibility {$K_{\phi,m}$}. The $K_{\phi,m}$ values were determined using the relation: $K_{\phi,m} = K_{s,2,\phi}/M$, where M is the molar mass of the solute. The $K_{\phi,m}$ values suggest the influence of the cosolute on the taste quality

DOI: 10.1021/acs.jced.9b00327
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of the solute and are divided into four basic tastes,[37] that is, salt: $K_{\phi,m}$ = (−2.332 × 10^{-5} to −8.064 × 10^{-5}) × 10^{-8} $m^3 \cdot kg^{-1} \cdot Pa^{-1}$; sweet: $K_{\phi,m}$ = (−3.383 × 10^{-7} to −2.335 × 10^{-5}) × 10^{-8} $m^3 \cdot kg^{-1} \cdot Pa^{-1}$; sour: $K_{\phi,m}$ = (6.131 × 10^{-6} to −2.991 × 10^{-5}) × 10^{-8} $m^3 \cdot kg^{-1} \cdot Pa^{-1}$; and bitter: $K_{\phi,m}$ = (−1.993 × 10^{-8} to −2.487 × 10^{-6}) × 10^{-8} $m^3 \cdot kg^{-1} \cdot Pa^{-1}$. The $K_{\phi,m}$ values of GABA in water at (293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K lie in the sour taste range (−2.96 × 10^{-5} to −1.73 × 10^{-5}) × 10^{-8} $m^3 \cdot kg^{-1} \cdot Pa^{-1}$. In aqueous solutions of CAF, the $K_{\phi,m}$ values for GABA are still in the sour taste range (−3.50 × 10^{-5} to −2.12 × 10^{-5}) × 10^{-8} $m^3 \cdot kg^{-1} \cdot Pa^{-1}$ at all the concentrations of CAF. The apparent specific volumes ν_ϕ of GABA in water lie in the bitter taste range (0.73−0.74) × 10^{-3} $m^3 \times kg^{-1}$, whereas for GABA in the presence of aqueous CAF, the ν_ϕ values lie in the sweet-bitter taste range (0.69−0.72) × 10^{-3} $m^3 \times kg^{-1}$.

UV−Visible Spectroscopy. The UV−visible absorption of CAF is mainly because of the $\pi-\pi$ * transition of the purine base. The structural effect of CAF on GABA molecules has been determined by performing UV absorption studies. The results have also been discussed in terms of hydrophilic and hydrophobic interactions. Aliquots (2 mL) of 5.0 × 10^{-6} M solutions of CAF have been titrated (50 μL additions) with 0.4 M GABA, which resulted in the gradual increase in absorbance (hyperchromic effect) (Figure 2). The observed increase in the absorption maxima may be attributed to the hydrophilic−hydrophilic interactions or the hydrogen-bonding interactions. Sirrajuddin et al.[39] studied the drug−DNA interactions and concluded that hyperchromism is the sign of electrostatic mode of interaction. CAF molecules have no hydrogen donor groups and therefore are unable to self-associate by H bonding directly. The effect in dilute solutions is interpreted as H-bonding CAF−water molecule interactions through polar groups, nitrogen atom (N9), or the two exocyclic carbonyl groups. In the presence of GABA, which is a proton donor as well as a proton acceptor, hyperchromic effect has been observed for CAF because of the increase in the number of molecules of GABA. The increase thus leads to the interaction behavior of CAF with GABA through H-bonding interactions, which leads to solute−cosolute interactions.

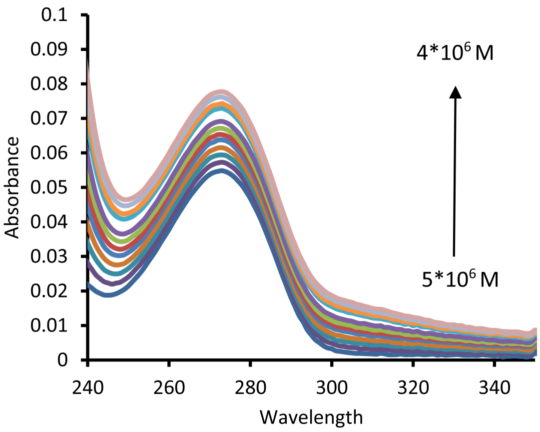

Figure 2. Absorbance plot for binding of CAF vs GABA.

Density Functional Theory. The optimized structures of GABA and CAF and their interactions in gas phase and in the presence of water as solvent are given in Figures 3 & 4. The various geometrical parameters of GABA and CAF are reported in Tables S1 and S2. It has been observed that the interaction energy of GABA and CAF in gas phase is 4.38 (3.37 ZPVE corrected) kcal/mol. It is increased to 17.08 (16.55 ZPVE corrected) kcal/mol in the presence of water as the solvent. This indicates the strong stabilization in water. Hydrogen-bonding interactions are the strongest noncovalent interactions. H-bond interaction has been anticipated in GABA and CAF as there are several atoms with lone pair of electrons and several polarized bonds. The shorter the distance from the sum of van der Waals radii and closer the angle to 180°, stronger is the H-bond interaction. There is a strong H-bond interaction between the N−H bond of GABA and the oxygen atom of CAF with the N−H···O bond distance of 2.147 Å (sum of van der Waals radii, 2.60) and bond angle of 161.11°. The H-bond interaction has also been observed in solvent phase with the N−H···O bond distance of 2.20 Å and angle of 170.33°. These H-bond interactions have also been supported from the elongation of C−O bond distance from 1.225 Å (CAF) to 1.235 Å during the interaction with GABA in gas phase and 1.237 Å in solution phase.

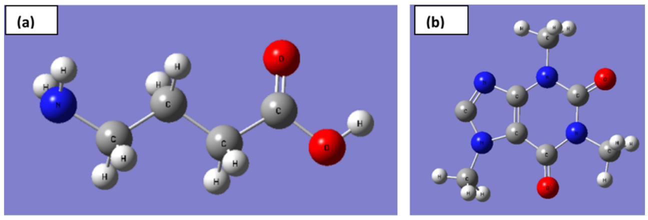

Figure 3. Optimized structures of (a) GABA and (b) CAF at B3LYP/6-31+G* theoretical level.

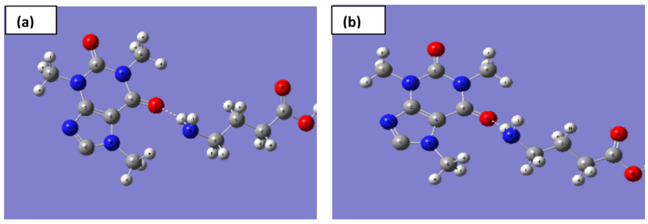

Figure 4. H-bond interactions of GABA and CAF (a) in gas phase and (b) in the presence of water as the solvent at B3LYP/6-31+G* theoretical level.

■ CONCLUSIONS

The volumetric properties, that is, density, ρ, and speed of sound, u, of GABA in water and in aqueous CAF solutions have been measured over the temperature range of (293.15−318.15) K. The negative transfer parameters, $\Delta_{tr}V^{o}_{2,\phi}$ and $\Delta_{tr}K^{o}_{s,2,\phi}$, reveal the dominance of hydrophobic type of interactions among the solute/cosolute/solvent system, that is, the GABA−CAF−water system. Moreover, Hepler's criteria from the negative values of $\partial^2 V^{o}_{2,\phi}/\partial T^2$ for GABA in water and in CAF also support its structure-breaking tendency. The ν_ϕ and $K_{\phi,m}$ values indicate the shift in the taste quality of GABA from bitter to sweet-bitter taste range in the presence of CAF.

UV−visible spectroscopic studies show an increase in the absorbance of CAF with the increase in the concentration of GABA, that is, the hyperchromic effect. This is attributed to the dominance of hydrogen-bonding interactions. The DFT results suggest the strong stabilization of hydrogen-bonding interactions between GABA and CAF as the interaction energy increased almost 4 times in the presence of water than in gas

DOI: 10.1021/acs.jced.9b00327
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phase. This is further supported by the decrease in the N−H···O bond distance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.9b00327.

Important geometrical parameters of GABA and CAF at B3LYP/6-31+G* level and comparison plots of density (ρ) and speed of sound (u) for (GABA + H_2O) and (CAF + H_2O) systems with the literature data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful to Guru Nanak Dev University, Amritsar, for providing the infrastructure for carrying out the research.

■ LIST OF SYMBOLS

M	molar mass of γ-aminobutyric acid
m_A	molality of γ-aminobutyric acid
m_B	molality of caffeine in water
λ	wavelength of sound waves
T	temperature
P	pressure
ρ_o	density of the solvent
ρ	density of the solution
$V^o_{2,\phi}$	apparent molar volumes at infinitesimal concentration
$\Delta_{tr}V^o_{2,\phi}$	apparent molar volumes of transfer at infinitesimal concentration
$V_{2,\phi}$	apparent molar volume
S_v	experimental slope
$(\partial V^o_{2,\phi}/\partial T)_P$	apparent molar expansibilities
$(\partial^2 V^o_{2,\phi}/\partial T^2)_P$	second derivative of partial molar volume
ν_ϕ	apparent massic volume
u	speed of sound
Z	acoustic impedance
κ^o_s	isentropic compressibility of solvent
κ_s	isentropic compressibility of solution
$K_{s,2,\phi}$	apparent molar isentropic compressibility
$K^o_{2,\phi}$	standard partial molar isentropic compressibility at infinite dilution
$\Delta_t K^o_{2,\phi}$	standard partial molar isentropic compressibility of transfer at infinite dilution
n_w	hydration number
$K_{\phi,m}$	apparent massic isentropic compressibility

List of Abbreviations

GABA	γ-aminobutyric acid
CAF	caffeine
DFT	density functional theory
CNS	central nervous system
SRL	Sisco Research Laboratories
DSA	density and sound velocity analyzer
PT-100	Peltier thermostat
ZPVE	zero-point vibrational energy
SCRF	self-consistent reaction field
SCI-PCM	self-consistent isodensity-polarized continuum model

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DOI: 10.1021/acs.jced.9b00327
J. Chem. Eng. Data XXXX, XXX, XXX−XXX