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Vanillin Schiff bases: Molecular interactions in methanol and THF solutions

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Summary

Density, ultrasonic velocity and viscosity of some vanillin Schiff bases derivatives have been studied in methanol and tetrahydrofuran (THF) at 308.15 K. From the experimental data, various acoustical parameters such as isentropic compressibility (κ_s), Rao's molar sound function (R_m), Van der Waals constant (b), relaxation strength (r), intermolecular free length (L_f), apparent molar compressibility, etc. have been evaluated, which helps in understanding the molecular interactions occurring in these solutions.

Keywords: Vanillin Schiff bases, ultrasonic Study, acoustical parameters, methanol, THF.

Resumen

Bases de Schiff de vainillina: interacciones intermoleculares en soluciones de metanol y THF

En este trabajo se estudiaron la densidad, la velocidad ultrasónica y la viscosidad de soluciones de algunas bases de Schiff derivadas de la vainillina en metanol y tetrahidrofurano (THF) a 308,15 K. A partir de los datos experimentales, se evaluaron diversos parámetros acústicos, como la compresibilidad isentrópica (κ_s), la función acústica molar de Rao (R_m), la constante de Van der Waals (b), la fuerza de relajación (r), la longitud intermolecular libre (L_f), la compresibilidad molar aparente, etc., todo lo cual ayuda a comprender las interacciones moleculares que ocurren en estas soluciones.

Palabras clave: bases Schiff de vainilla, estudio ultrasónico, parámetros acústicos, metanol, THF.

Introduction

Ultrasonic velocity measurements have been used to study the nature of molecular interactions in various pure liquids [1-3], liquid mixtures [4-10] and in solutions [11-17]. However, little work has been done for some organic compound solutions [18-21] especially Schiff bases [22-25].

Some of these bases are known to possess a wide spectrum of biological activities and are used in pharmaceutical science [26-29]. The presence of different functional groups cause different type of interactions with different solvents which is an important parameter for the selection of these compounds as starting material, intermediate or product [30-32]. Further, binding or interaction of a compound or drug affects their pharmacokinetic and pharmacodynamic properties [33-35]. For the prediction of biological activities and transport phenomena also, physiochemical parameters are required [36, 37] and one of important parameter is interaction between solute and solvent molecules. The ultrasonic study is one of the non-destructive tools to study different types of interactions occurring in solutions [38, 39].

Thus, in present paper, acoustical properties of some vanillin Schiff bases are studied in methanol and THF over entire concentration range at 308.15 K. The results are interpreted in terms of molecular interactions occurring in the solution.

Experimental

The methanol and THF used in the present work were of AR grade and were purchased from Spectrochem Pvt. Ltd (Mumbai) and were purified according to the standard procedure [40]. The Schiff bases were synthesized in the laboratory and were recrystallized before use. The common structure of synthesized Schiff bases and their substitution groups (R) are given in Figure 1.

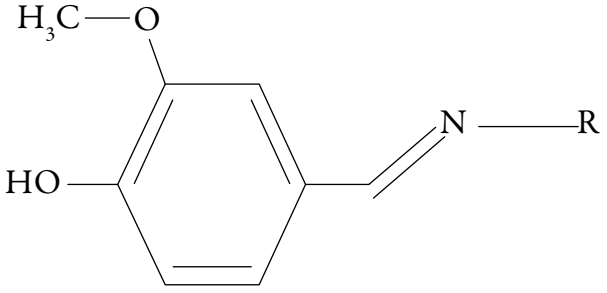

Figure 1. General structure of vanillin Schiff bases. **R is:** ***SV-1***: 4-CH_3-C_6H_4; ***SV-2***: 3-Cl-4-F-C_6H_3; ***SV-3***: 3-OCH_3-C_6H_4; ***SV-4***: 4-F-C_6H_4; ***SV-5***: 2-CH_3-C_6H_4; ***SV-6***: 2-Cl,5-Cl-C_6H_3; ***SV-7***: -C_6H_5; ***SV-8***: -$C_5H_6N_3O$-C_6H_5.

The densities, ultrasonic velocity and viscosity of pure solvents and their solutions were measured by single capillary pycnometer, single crystal variable path ultrasonic interferometer operating at 2 MHz (Mittal Enterprises) and Ubbelohde viscometer respectively. The accuracy of density, velocity and viscosity are ± 0.0001 g/cm^3, ± 0.1% cm/sec and 0.05% respectively. All the measurements were carried out at 308.15 K. The uncertainty of temperature is ± 0.1 K and that of concentration is 0.0001 mol/dm^3.

Results and discussion

The experimental data of ultrasonic velocity, density and viscosity are given in Table 1.

Table 1. The density (ρ), ultrasonic velocity (U) and viscosity (η) of vanillin Schiff bases in methanol and THF at 308.15 K.

Conc. (M)	Density g.cm^{-3}	Velocity × 10^{-5} cm.s^{-1}	Viscosity × 10^3 poise	Density g.cm^{-3}	Velocity × 10^{-5} cm.s^{-1}	Viscosity × 10^3 poise
Methanol				THF		
SV-1						
0.01	0.7768	1.0848	5.0285	0.8784	1.2416	4.6053
0.02	0.7782	1.0872	5.0690	0.8797	1.2424	4.6492
0.04	0.7796	1.0896	5.1500	0.8806	1.2432	4.7259
0.06	0.7814	1.0936	5.3060	0.8815	1.2452	4.8505
0.08	0.7821	1.0956	5.3475	0.8819	1.2468	4.8898
0.10	0.7831	1.0972	5.4449	0.8829	1.2488	4.9811
SV-2						
0.01	0.7777	1.0812	5.0393	0.8802	1.2400	4.6205
0.02	0.7794	1.0836	5.0945	0.8811	1.2404	4.6715
0.04	0.7803	1.0852	5.1433	0.8815	1.2408	4.7150
0.06	0.7812	1.0872	5.2510	0.8823	1.2420	4.8178
0.08	0.7827	1.0884	5.5257	0.8830	1.2432	5.0659
0.10	0.7842	1.0912	5.7881	0.8839	1.2444	5.2920
SV-3						
0.01	0.7778	1.0860	5.1268	0.8810	1.2404	4.7237
0.02	0.7798	1.0880	5.2188	0.8821	1.2412	4.7960
0.04	0.7812	1.0916	5.2705	0.8824	1.2428	4.8390
0.06	0.7824	1.0960	5.3318	0.8827	1.2432	4.9114
0.08	0.7826	1.0996	5.4364	0.8830	1.2448	4.9923
0.10	0.7836	1.1032	5.5562	0.8838	1.2456	5.0969

(*Continuous*)

Table 1. The density (ρ), ultrasonic velocity (U) and viscosity (η) of vanillin Schiff bases in methanol and THF at 308.15 K (*continuation*).

Conc. (M)	Density g.cm^{-3}	Velocity $\times 10^{-5}$ cm.s^{-1}	Viscosity $\times 10^{3}$ poise	Density g.cm^{-3}	Velocity $\times 10^{-5}$ cm.s^{-1}	Viscosity $\times 10^{3}$ poise
Methanol				THF		
SV-4						
0.01	0.7773	1.0876	5.0361	0.8798	1.2400	4.6547
0.02	0.7781	1.0904	5.0853	0.8805	1.2404	4.6961
0.04	0.7787	1.0924	5.1283	0.8808	1.2412	4.7255
0.06	0.7798	1.0940	5.1835	0.8811	1.2424	4.8048
0.08	0.7824	1.0992	5.3084	0.8821	1.2428	4.9109
0.10	0.7826	1.1016	5.4395	0.8842	1.2468	5.0435
SV-5						
0.01	0.7764	1.0852	5.0121	0.8786	1.2400	4.5630
0.02	0.7778	1.0868	5.0299	0.8788	1.2407	4.6153
0.04	0.7785	1.0880	5.0836	0.8796	1.2412	4.6771
0.06	0.7793	1.0912	5.1197	0.8805	1.2420	4.7538
0.08	0.7807	1.0940	5.1977	0.8819	1.2424	4.8391
0.10	0.7815	1.0984	5.3029	0.8829	1.2436	4.9275
SV-6						
0.01	0.7769	1.0816	5.2271	0.8784	1.2420	4.8462
0.02	0.7790	1.0836	5.3855	0.8797	1.2432	4.9516
0.04	0.7804	1.0864	5.5234	0.8806	1.2444	5.0878
0.06	0.7853	1.0900	5.6686	0.8815	1.2469	5.1906
0.08	0.7873	1.0924	5.8021	0.8819	1.2476	5.2993
0.10	0.7885	1.0964	5.8862	0.8829	1.2500	5.3782
SV-7						
0.01	0.7774	1.0848	5.2455	0.8792	1.2396	4.8585
0.02	0.7784	1.0896	5.3631	0.8795	1.2408	4.9640
0.04	0.7789	1.0936	5.4466	0.8812	1.2420	5.0527
0.06	0.7806	1.0964	5.4995	0.8813	1.2432	5.0889
0.08	0.7815	1.0988	5.6108	0.8823	1.2448	5.1946
0.10	0.7819	1.1012	5.7490	0.8830	1.2476	5.3288

(*Continuous*)

Table 1. The density (ρ), ultrasonic velocity (U) and viscosity (η) of vanillin Schiff bases in methanol and THF at 308.15 K (*continuation*).

Conc. (M)	Density g.cm^{-3}	Velocity × 10^{-5} cm.s^{-1}	Viscosity × 10^{3} poise	Density g.cm^{-3}	Velocity × 10^{-5} cm.s^{-1}	Viscosity × 10^{3} poise
Methanol				THF		
SV-8						
0.01	0.7767	1.0852	5.2917	0.8795	1.2424	4.5791
0.02	0.7782	1.0904	5.4127	0.8812	1.2436	4.6357
0.04	0.7786	1.0948	5.4810	0.8817	1.2448	4.6997
0.06	0.7792	1.0972	5.5401	0.8824	1.2476	4.7862
0.08	0.7799	1.1004	5.6214	0.8831	1.2488	4.8664
0.10	0.7806	1.1036	5.7395	0.8839	1.2520	4.9724

From the experimental data, various acoustical parameters were calculated using equations reported earlier [41].

Figure 2 shows the variation of ultrasonic velocity (U) increases with concentration for all the compounds in methanol and THF. It is observed that ultrasonic velocity increases with concentration for all the compounds in both the solvents.

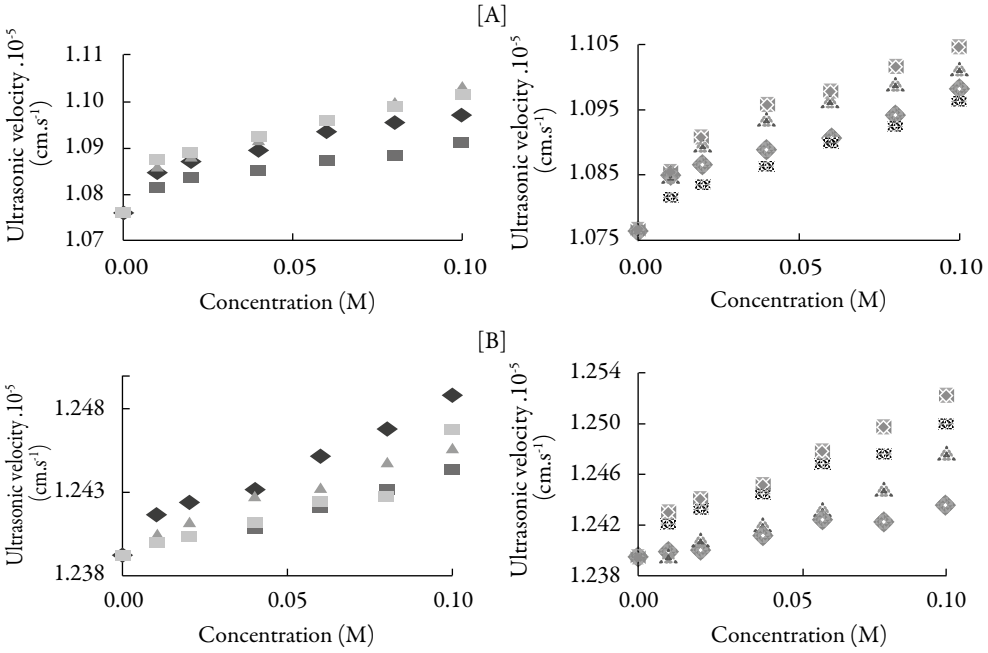

Figure 2. The variation of ultrasonic velocity with concentration in [A] methanol and [B] THF. ◆: **SV-1**, ■: **SV-2**, ▲: **SV-3**, ■: **SV-4**, ◆: **SV-5**, ▩: **SV-6**, ▲: **SV-7**, ▩: **SV-8**.

The velocity depends on intermolecular free length (L_f). Figure 3 show that L_f decreases continuously with concentration. Thus, intermolecular free length is reverse of velocity. In a solution, when the distance between molecules of solvent and compound decreases, L_f decreases which causes velocity to increase. The decrease in distance suggests interaction between solvent and compound molecules.

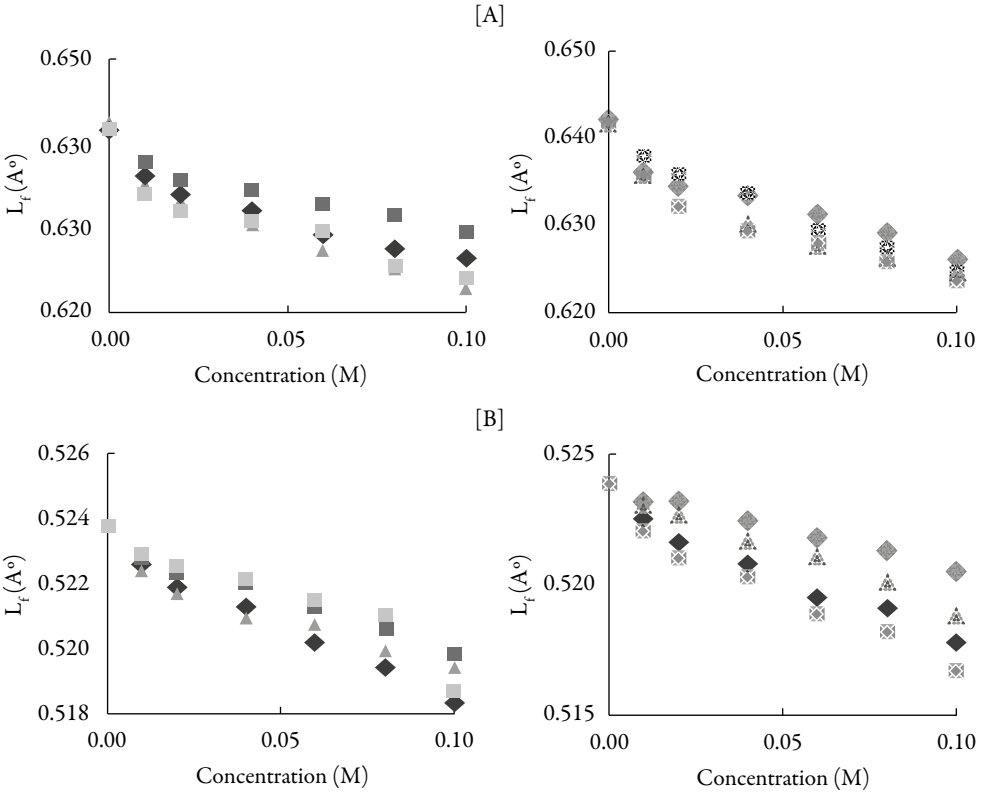

Figure 3. The variation of intermolecular free path length (L_f) with concentration in [A] methanol and [B] THF. ◆: **SV-1**, ■: **SV-2**, ▲: **SV-3**, ■: **SV-4**, ◆: **SV-5**, ■: **SV-6**, ▲: **SV-7**, ■: **SV-8**.

This is further supported by isentropic compressibility (κ_s) and relaxation strength (r). The variation of these two parameters with concentration of these compounds is also shown in Figures 4 and 5.

It is observed that both isentropic compressibility and relaxation strength decrease with concentration for all the compounds in both the solvents. The decrease of isentropic compressibility and relaxation strength with increasing concentration might be due to aggregation of solvent molecules around compound molecules which causes interaction between molecules of compound and solvent.

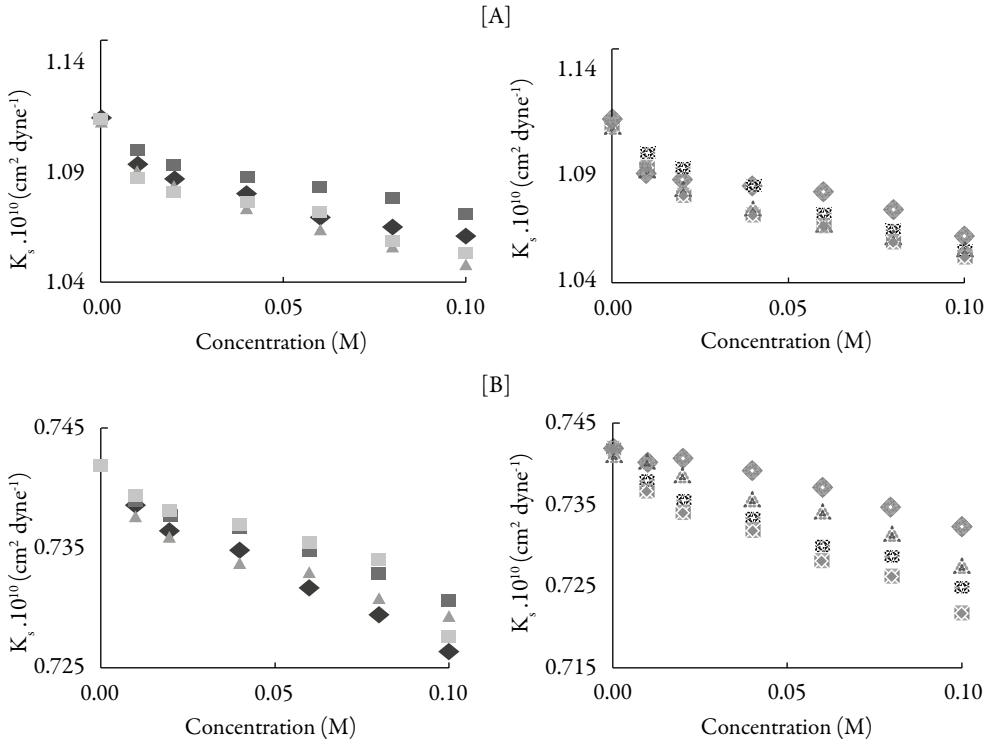

Figure 4. The variation of isentropic compressibility (κ_s) with concentration in [A] methanol and [B] THF.◆: **SV-1**, ■: **SV-2**, ▲: **SV-3**, ■: **SV-4**, ◈: **SV-5**, ▩: **SV-6**, ◬: **SV-7**, ▩: **SV-8**.

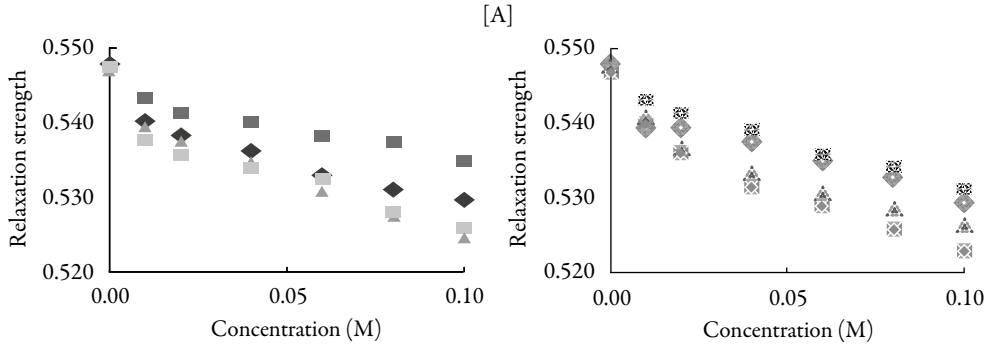

Figure 5. The variation of relaxation strength with concentration in [A] methanol and[B] THF. ◆: **SV-1**, ■: **SV-2**, ▲: **SV-3**, ■: **SV-4**, ◈: **SV-5**, ▩: **SV-6**, ◬: **SV-7**, ▩: **SV-8**. (*Continuous*)

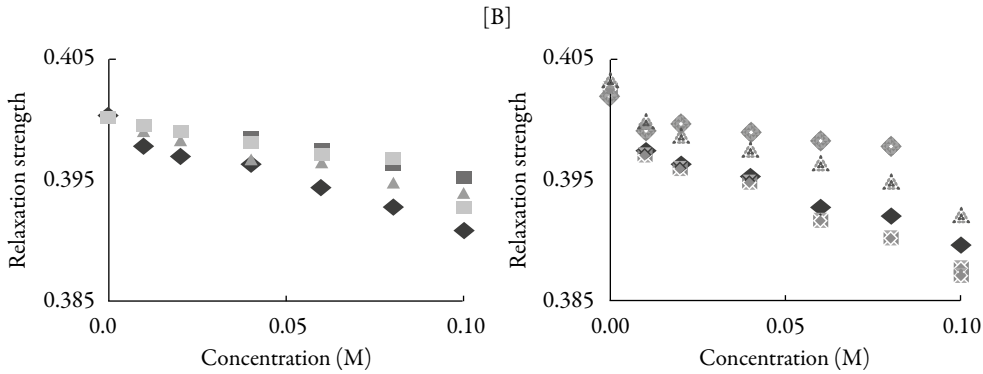

Figure 5. The variation of relaxation strength with concentration in [A] methanol and[B] THF (*continuation*). ◆: **SV-1**, ■: **SV-2**, ▲: **SV-3**, ■: **SV-4**, ◆: **SV-5**, ▩: **SV-6**, ▲: **SV-7**, ▩: **SV-8**.

For all the compounds in both the solvents, Rao's molar sound function (R_m), molar compressibility (W) and Van der Waals' constant (b) vary linearly with concentration. Table 2 shows the correlation equation and correlation coefficient values for all these solutions. The linear change indicates that there is no complex formation in solution.

Table 2. The least-square Correlation equations and Correlation coefficients (γ) for compounds in methanol and THF at 303.15 K. C is the concentration.

Parameters	Correlation Equation	γ	Correlation equation	γ
	Methanol		THF	
SV-1				
$W.10^{-3}$ (cm^{-1} . $dyne^{-1}$)	2.2434 C + 1.0915	0.9999	1.3947 C + 2.3278	0.9998
R_m. 10^{-3}($cm^{-8/3}$. $s^{-1/3}$)	3.8495 C + 1.9647	1	2.4623 C + 4.1452	0.9997
b (cm^3 . mol^{-1})	78.104 C + 41.244	0.9999	47.335 C + 83.125	0.9996
SV-2				
$W.10^{-3}$ (cm^{-1} . $dyne^{-1}$)	2.921 C + 1.0901	1	1.978 C + 2.3253	0.9996
R_m. 10^{-3} ($cm^{-8/3}$. $s^{-1/3}$)	5.2374 C + 1.9625	1	3.3422 C + 4.1541	0.9812
b (cm^3 . mol^{-1})	108.01 C + 41.223	0.9999	68.89 C + 83.036	0.9993
SV-3				
$W.10^{-3}$ (cm^{-1} . $dyne^{-1}$)	2.4878 C + 1.0898	0.9999	1.6347 C + 2.3238	0.9985
Rm . 10^{-3} ($cm^{-8/3}$. $s^{-1/3}$)	4.4708 C + 1.962	0.9999	2.8892 C + 4.1369	0.9979
b (cm^3 . mol^{-1})	90.274 C + 41.19	0.9997	49.312 C+ 83.082	0.9986

(*Continuous*)

Table 2. The least-square Correlation equations and Correlation coefficients (γ) for compounds in methanol and THF at 303.15 K (*continuation*).

Parameters	Correlation Equation	γ	Correlation equation	γ
	Methanol		THF	
SV-4				
$W.10^{-3}$ (cm^{-1} . $dyne^{-1}$)	2.2434 C + 1.0915	0.9999	1.4368 C + 2.3262	0.9993
R_m . 10^{-3} ($cm^{-8/3}$. $s^{-1/3}$)	4.307 C + 1.9594	0.9946	2.5345 C + 4.1419	0.9991
b (cm^3 . mol^{-1})	81.488 C + 41.248	0.9999	49.312 C + 83.082	0.9986
SV-5				
$W.10^{-3}$ (cm^{-1} . $dyne^{-1}$)	2.1744 C + 1.0911	1	1.3677 C + 2.3284	0.9999
R_m . 10^{-3} ($cm^{-8/3}$. $s^{-1/3}$)	3.9085 C + 1.9649	0.9999	2.4071 C + 4.1465	0.9998
b (cm^3 . mol^{-1})	79.365 C + 41.255	1	47.335 C + 83.125	0.9996
SV-6				
$W.10^{-3}$ (cm^{-1} . $dyne^{-1}$)	3.229 C + 1.0916	0.9999	2.3194 C + 2.3281	0.9999
R_m . 10^{-3} ($cm^{-8/3}$. $s^{-1/3}$)	5.7712 C + 1.9657	0.9998	4.1109 C + 4.1458	0.9999
b (cm^3 . mol^{-1})	118.3 C + 41.3	0.9999	47.335 C + 83.125	0.9996
SV-7				
$W.10^{-3}$ (cm^{-1} . $dyne^{-1)}$	2.4848 C + 1.0909	1	1.6207 C + 2.3266	0.9997
R_m . 10^{-3} ($cm^{-8/3}$. $s^{-1/3}$)	4.4705 C + 1.9643	1	2.865 C + 4.1428	0.9996
b (cm^3 . mol^{-1})	90.515 C + 41.227	0.9999	55.573 C + 83.101	0.9996
SV-8				
$W.10^{-3}$ (cm^{-1} . $dyne^{-1}$)	4.5052 C + 1.0911	1	3.1409 C + 2.3263	0.9999
R_m . 10^{-3} ($cm^{-8/3}$. $s^{-1/3}$)	8.1169 C + 1.9647	1	5.5731 C + 4.1422	0.9998
b (cm^3 . mol^{-1})	166.23 C + 41.239	1	108.9 C + 83.056	0.9998

The type and magnitude of interactions in solution is further confirmed by apparent molar properties. The apparent molar compressibility's (ϕ_k) of the solutions is fitted to Gucker's relation [42].

$$\phi_k = \phi^o_k + S_k \sqrt{C}$$

From the plot of ϕ_k verses $\sqrt{C}$, ϕ^o_k and S_k values are evaluated from the intercept and slope. The isentropic compressibility of all the solutions was also fitted to the following Bachem's relation [43]:

$$k_s = k_s^0 + AC + BC^{3/2}$$

The values of A and B were evaluated from the intercept and slope respectively. k_s^0 is the isentropic compressibility of pure solvent. All these values of intercept and slopes are given in Table 3.

Table 3. Constants A, B, ϕ^o_k and S_k for vanillin Schiff bases in methanol and THF at 308.15 K.

Compound Code	$A \times 10^{11}$ $dyn^{-1}.cm^3.mol^{-1}$	$B \times 10^{11}$ $dyn^{-1}.cm^{-1/2}.mol^{-3/2}$	$\phi^o_k \times 10^8$ $dyn^{-1}.mol^{-1}$	$S_k \times 10^8$ $dyn^{-1}cm^{-3/2}.mol^{3/2}$
		Methanol		
SV-1	-13.70	30.0	-12.80	30.01
SV-2	-10.02	20.5	-9.54	28.01
SV-3	-15.20	26.6	-16.20	43.33
SV-4	-15.90	33.3	-14.02	61.53
SV-5	-11.20	20.5	-8.85	30.72
SV-6	-14.01	27.3	-13.21	32.05
SV-7	-17.40	38.0	-15.20	40.04
SV-8	-18.90	45.0	-16.80	32.25
		THF		
SV-1	-4.25	10.0	-9.80	3.24
SV-2	-3.65	10.0	0.19	0.51
SV-3	-3.75	10.1	-2.82	10.6
SV-4	-3.25	10.0	-2.60	10.9
SV-5	-1.16	0.9	0.75	0.36
SV-6	-4.49	10.4	-3.24	12.1
SV-7	-1.71	1.0	-0.84	2.55
SV-8	-3.55	4.3	-2.52	1.01

Table 3 shows that in both solvents A and ϕ^o_k values are negative or very low whereas B and S_k values are positive. The low or negative A and ϕ^o_k values and positive B and S_k values suggest predominance of solute-solvent interactions.

Conclusions

It is concluded that in studied solutions of vanillin Schiff bases, compound-solvent interactions exist. This suggests that these compounds are more bonded to solvent and some modification is required so that it can easily be absorbed by the target.

Disclosure statement

No potential conflict of interest was reported by the authors.

Acknowledgments

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