Partial Molar Volumes of *N*,*N′*-1,2-Ethyl-bis(salicyladimine) Schiff Base (Salen) in Organic Solvents at $T = (283.15 \text{ to } 318.15)$ K

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Densities of *N*,*N′*-1,2-ethyl-bis(salicyladimine) Schiff base (salen) in dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), dichloromethane (CH_2Cl_2), and chloroform ($CHCl_3$) binary mixtures have been measured in dilute concentration regions of salen at $T = (283.15$ to $318.15)$ K under ambient pressure. Apparent molar volumes, V_ϕ, and standard partial molar volumes, V_ϕ^0, have been calculated from the measured densities. The V_ϕ^0 values in DMSO have larger values corresponding to the high polarity of this solvent. The results show that their values would be increased slightly with an increase in temperature. The partial molar expansivities, E_ϕ^0, and the isobaric thermal expansion coefficients, α^*, have been calculated from the temperature dependence of V_ϕ^0 values. The Hepler's constant values, $(\partial^2 V_\phi^0/\partial T^2)_p$, were found to be positive or very small and negative which indicate that salen Schiff base is predominately a structure maker in all organic solvents studied.

Introduction

Schiff bases, the molecules that can be prepared from the condensation of aldehydes, ketones, and β-diketones reacting with primary amines and related derivatives and formation imine functional groups, are considered a class of very important ligands in the growth of coordination chemistry.[1−3] Because of the versatility of their steric and electronic properties, which can be fine-tuned by choosing the appropriate amine and the substituents on an aromatic ring of the carbonyl compound, transition metal complexes with a Schiff base are widely studied.[2] Such ligands possess interesting photophysical properties with potential applications as organic materials for reversible optical data storage.[4] Although many structures of transition metal complexes with Schiff base ligands have been determined, a relatively small number of free Schiff bases have been structurally characterized.[5] The salen type ligands of Schiff base are among the oldest high diversity ligands in coordination chemistry that were used in catalytic reactivity, thermochromism behaviors, solvatochromism behaviors, mechanochromism behaviors, single molecular magnetism (SMM), sensors, and biological properties.[6−11] In spite of their important applications, a literature survey revealed that studies on the solute−solvent interactions in various organic solvents are scarce. Considering the fact those volumetric properties of mixtures can provide valuable information about solute−solvent and solute−solute interactions in solution, herein the volumetric properties of salen in organic solvents have been measured to understand the effect of organic solvents with different polarities on the solute−solvent interactions in these types of solutions.[12,13]

For this purpose, the densities of a salen Schiff base with several organic solvents with a different range of polarity, dimethylsulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMA), *N*,*N*-dimethylformamide (DMF), dichloromethane (CH_2Cl_2), and chloroform ($CHCl_3$) in the dilute concentration region at several temperatures have been measured. Using these data, the apparent molar volumes, V_ϕ, standard partial molar volumes, V_ϕ^0, and partial molar expansivities, E_ϕ^0, and the isobaric thermal expansion coefficients, R^*, have been calculated. The obtained volumetric quantities have been used to interpret of solute−solvent and solute−solute interactions occurring in these types of binary mixtures.

Experimental Section

Chemicals. Reagents used in work were DMSO (> 99.9 %, in mass fraction), DMF (> 99 %, in mass fraction), DMA (> 99 % in mass fraction), chloroform (> 99.4 %, in mass fraction), dichloromethane (> 99.8 %, in mass fraction), 1,2-ethylenediamine, and 2-hydroxybenzaldehyde obtained from Merck. These chemicals were used without further purification. During the course of the experiments, the purity of solvents was monitored by density measurements. The density and refractive index values of the pure solvents are given in Table 1 and compared with the literature values.[14−23]

Experimental Procedure. The mass of chemicals were determined using a Sartorius AG TE214S analytical balance with a precision of $\pm 1 \cdot 10^{-4}$ g. The solutions were prepared in molal base by filling glass vials with organic solvent and salen Schiff base ligand and are closed tightly to avoid moisture. The uncertainty in the molality of the solutions was estimated to be better than ± 0.0002 mol·kg^{-1}. The sample was taken from the vial with a syringe and injected immediately into the densimeter. Density data were continuously measured using a vibrating tube densimeter (model DMA 4500M, Anton Paar). The densimeter was calibrated with doubly distilled and degassed water and dried air at atmospheric pressure. The temperature was automatically kept constant with an accuracy of $1 \cdot 10^{-3}$ K using the built-in Peltier technique. The accuracy of the apparatus performance was also tested with the density of a known molality of aqueous NaCl using the data given by Pitzer.[24] For all of the samples, the estimated precision of the

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Table 1. Densities, *d*, and Refractive Indices, n_D, of Pure Organic Solvents

		$10^{-3}\cdot d/\mathrm{kg\cdot m^{-3}}$		n_D	
solvent	T/K	exp.	lit.	exp.	lit.
DMSO	288.15	1.10530		1.4793	
	298.15	1.09529	1.09532[a]	1.4752	1.4775[a]
	308.15	1.08525	1.08533[a]	1.4710	1.4729[a]
	318.15	1.07521		1.4670	
DMA	288.15	0.94550	0.944267[b]	1.4382	
	298.15	0.93628	0.935287[b]	1.4346	1.4363[c]
	308.15	0.92705	0.926297[b]	1.4312	1.4319[c]
	318.18	0.91779	0.917216[b]	1.4260	
DMF	288.15	0.95358		1.4310	
	298.15	0.94406	0.9445[d]	1.4276	1.4289[e]
	308.15	0.93452	0.9351[d]	1.4230	1.4245[c]
	318.15	0.92490		1.4180	
CH_2Cl_2	283.15	1.34365		1.4305	
	288.15	1.33457	1.33451[f]	1.4276	
	293.15	1.32543	1.32564[f]	1.4251	
	298.15	1.31627	1.31640[f]	1.4219	1.42116[g]
$CHCl_3$	283.15	1.49643	1.5073[h]	1.4500	1.45189[h]
	288.15	1.48709		1.4471	
	293.15	1.47768	1.4884[h]	1.4439	1.44589[h]
	298.15	1.46828	1.47899[i]	1.4420	1.44290[j]

[a] Ref 15. [b] Ref 14. [c] Ref 22. [d] Ref 17. [e] Ref 23. [f] Ref 18. [g] Ref 20. [h] Ref 21. [i] Ref 16. [j] Ref 19.

Table 2. Experimental Values of Density, $d/\mathrm{kg\cdot m^{-3}}$, and Apparent Molar Volume, $V_\phi/\mathrm{m^3\cdot mol^{-1}}$, as a Function of Salen Molality, $m/\mathrm{mol\cdot kg^{-1}}$, in Organic Solvents at Various Temperatures

	T/K = 288.15		T/K = 298.15		T/K = 308.15		T/K = 318.15	
m	$10^{-3}\cdot d$	$10^6\cdot V_\phi$	$10^{-3}\cdot d$	$10^6\cdot V_\phi$	$10^{-3}\cdot d$	$10^6\cdot V_\phi$	$10^{-3}\cdot d$	$10^6\cdot V_\phi$
Salen + DMSO								
0.0098	1.10542	232.73	1.09542	233.92	1.08539	235.11	1.07536	236.31
0.0300	1.10567	232.58	1.09569	233.77	1.08568	234.97	1.07567	236.18
0.0502	1.10593	232.34	1.09596	233.70	1.08597	234.90	1.07598	236.10
0.0697	1.10618	232.24	1.09623	233.53	1.08626	234.72	1.07628	236.04
0.0903	1.10645	232.08	1.09652	233.35	1.08656	234.63	1.07660	235.92
0.1097	1.10671	231.93	1.09679	233.25	1.08685	234.50	1.07690	235.85
0.1300	1.10699	231.76	1.09708	233.11	1.08714	234.49	1.07722	235.73
0.1502	1.10728	231.54	1.09739	232.86	1.08745	234.32	1.07756	235.49
0.1701	1.10755	231.45	1.09766	232.85	1.08775	234.22	1.07784	235.59
0.1893	1.10781	231.37	1.09791	232.87	1.08803	234.16	1.07813	235.56
Salen + DMA								
0.0298	0.94692	230.11	0.93772	231.08	0.92851	232.03	0.91927	232.99
0.0503	0.94790	229.83	0.93872	230.64	0.92952	231.68	0.92029	232.71
0.0704	0.94886	229.54	0.93969	230.44	0.93050	231.50	0.92129	232.40
0.0902	0.9498	229.42	0.94066	230.12	0.93148	231.19	0.92228	232.13
0.1100	0.95076	229.03	0.94160	230.11	0.93243	231.19	0.92325	232.06
0.1300	0.95171	228.83	0.94256	229.91	0.93341	230.90	0.92423	231.90
0.1510	0.95273	228.47	0.94357	229.71	0.93441	230.87	0.92525	231.81
0.1699	0.95361	228.44	0.94449	229.45	0.93535	230.53	0.92619	231.55
0.1898	0.95455	228.25	0.94543	229.33	0.93628	230.54	0.92714	231.50
Salen + DMF								
0.0302	0.95499	229.61	0.94549	230.65	0.93597	231.69	0.92638	232.35
0.049	0.95587	229.38	0.94639	230.24	0.93688	231.33	0.92729	232.43
0.0701	0.95686	229.11	0.94739	230.08	0.93789	231.21	0.92832	232.19
0.0913	0.95785	228.89	0.94839	229.92	0.93890	231.07	0.92935	231.98
0.1101	0.95872	228.79	0.94927	229.84	0.93979	230.99	0.93025	231.94
0.1238	0.95936	228.62	0.94991	229.75	0.94044	230.87	0.93091	231.82
0.1483	0.96050	228.39	0.95105	229.61	0.94160	230.69	0.93208	231.69
0.1702	0.96148	228.44	0.95208	229.40	0.94263	230.56	0.93314	231.45
0.1886	0.96235	228.14	0.95294	229.23	0.94348	230.50	0.93399	231.48
	T/K = 283.15		T/K = 288.15		T/K = 293.15		T/K = 298.15	
Salen + CH_2Cl_2								
0.0306	1.34232	224.01	1.33332	224.22	1.32426	224.42	1.31518	224.61
0.0490	1.34150	224.35	1.33254	224.65	1.32356	224.47	1.31450	224.99
0.0703	1.34058	224.40	1.33167	224.71	1.32269	225.10	1.31371	225.31
0.0903	1.33965	224.90	1.33082	225.01	1.32191	225.23	1.31295	225.64
0.1103	1.33877	225.01	1.32993	225.45	1.32106	225.73	1.31216	226.06
0.1301	1.33788	225.22	1.32912	225.49	1.32031	225.70	1.31143	226.14
0.1500	1.33701	225.31	1.32826	225.72	1.31950	225.94	1.31067	226.35
Salen + $CHCl_3$								
0.0099	1.49546	222.82	1.48615	223.13	1.47677	223.44	1.46741	223.28
0.0300	1.49353	222.92	1.48427	223.38	1.47497	223.37	1.46566	223.67
0.0498	1.49163	223.07	1.48244	223.36	1.47319	223.56	1.46395	223.74
0.0702	1.48969	223.19	1.48056	223.48	1.47136	223.77	1.46215	224.19
0.0904	1.48779	223.28	1.47871	223.61	1.46956	223.95	1.46041	224.33
0.1102	1.48595	223.34	1.47692	223.69	1.46784	223.97	1.45874	224.36
0.1336	1.48373	223.64	1.47475	224.04	1.46571	224.41	1.45668	224.78
0.1501	1.48228	223.50	1.47337	223.82	1.46438	224.16	1.45537	224.6
0.1900	1.47869	223.65	1.46985	224.06	1.46093	224.50	1.45205	224.85

density measurements was better then $\pm\, 2\cdot 10^{-5}\ \mathrm{g\cdot cm^{-3}}$. Details of measurement method are also given elsewhere.[25]

Refractive indices of the organic solvents were determined using a Abbe digital refractometer (ATAGO-DRA1, Japan) with an uncertainty of $\pm\, 1\cdot 10^{-4}$. The instrument was calibrated with doubly distilled water before each measurement. A procedure called "zero setting" was always performed before the actual measurements of the sample's refractive index, to ensure that the refractometer is working properly. The calibration was also checked with pure liquids of a known refractive index. The temperature was controlled using a circulating bath thermostat (Julabo model ED, Germany) with a stability of ± 0.01 K.

Results and Discussion

Volumetric Properties. The densities, d, of (salen + DMSO), (salen + DMF), (salen + DMA), (salen + dichloromethane), and (salen + chloroform) binary mixtures were measured as a function of salen molality, m, at $T = (283.15 \text{ to } 318)$ K. The apparent molar volumes, V_ϕ, of salen in the organic solvents were calculated from the density data using the following equation,[26]

$$V_\phi = \frac{M}{d} - \frac{(d - d_0)}{mdd_0} \tag{1}$$

where M is the molar mass of the salen, m is the molality of the salen in organic solvent, and d and d_0 are densities of solution and pure organic solvent, respectively. The calculated apparent molar volumes, V_ϕ, and densities of solutions are given in Table 2. Figure 1 shows the molal concentration dependence of V_ϕ values for salen in DMSO at several temperatures. As can be seen from Figure 1, there is a linear correlation between apparent molar volumes and concentration of salen at all experimental temperatures. The similar trend was also observed for the other studied binary mixtures of salen. The dependence of apparent molar volumes on the temperature is slightly positive for all of the solvents, though the experimental errors are large compared with difference by temperature, as seen in Table 2. The comparison of apparent molar volumes for the salen in the organic solvents was also depicted in Figure 2 at 298.15 K.

The apparent molar volume values were found to be adequately represented by the linear equation,

$$V_\phi = V_\phi^0 + S_v m \tag{2}$$

where V_ϕ^0 is the partial molar volume at infinite dilution that equals the standard partial molar volume. The values of V_ϕ^0 and S_v have been calculated by weighted least-squares regression analysis. The values of V_ϕ^0 and S_v along with their standard errors are listed in Table 3. The sign of S_v shows the nature of the solute−solute interactions, while V_ϕ^0 values reflect the presence of solute−solvent interactions.[27,28] The standard partial molar volumes, V_ϕ^0, are much greater than those of S_v values for all of the investigated solutions, which suggests that the solute−solvent

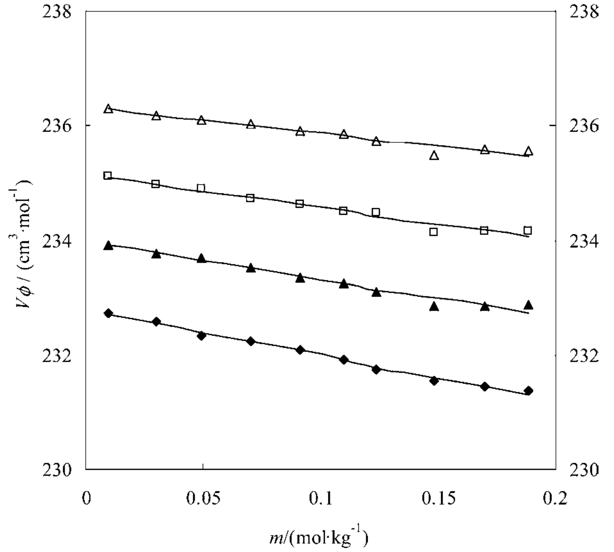

Figure 1. Apparent molar volumes, V_ϕ, of the (DMSO + salen) system as a function of salen concentration at experimental temperatures. ◆, 288.15 K; ▲, 298.15 K; □, 308.15 K; △, 318.15 K.

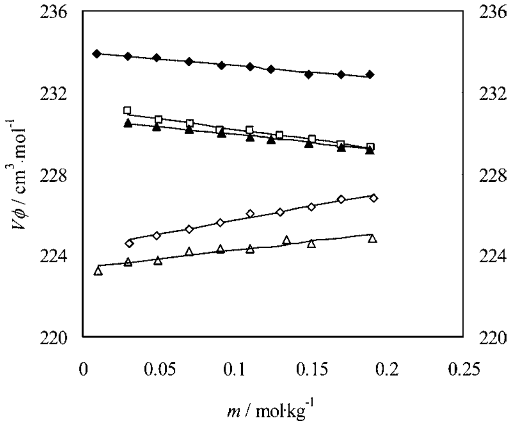

Figure 2. Apparent molar volumes, V_ϕ, of salen in organic solvents as a function of salen concentration at the experimental temperature of 298.15 K. ◆, DMSO; □, DMA; ▲, DMF; ◇, CH_2Cl_2; △, $CHCl_3$.

Table 3. Values of the Standard Partial Molar Volume of Salen, V^0_ϕ/m^3·mol^{-1}, Slope, S_v/m^3·mol$^{-3/2}$·kg$^{1/2}$, Correlation Coefficients, R^2, and Standard Deviation, S_d, for the Salen + Organic Solvent Binary Mixtures at Various Experimental Temperatures

T/K	$10^6\cdot V^0_\phi$	$10^6\cdot S_v$	R^2 (V_ϕ)	S_d (V_ϕ)
		Salen + DMSO		
288.15	232.78 ± 0.03	−7.8 ± 0.2	0.9935	0.04
298.15	233.97 ± 0.04	−6.5 ± 0.3	0.9726	0.07
308.15	235.13 ± 0.02	−5.3 ± 0.1	0.9893	0.03
318.15	236.33 ± 0.04	−4.5 ± 0.4	0.9506	0.07
		Salen + DMA		
288.15	230.42 ± 0.07	−11.9786 ± 0.548	0.9856	0.08
298.15	231.21 ± 0.08	−10.1963 ± 0.651	0.9723	0.10
308.15	232.17 ± 0.08	−9.1390 ± 0.675	0.9632	0.10
318.15	233.11 ± 0.08	−9.0849 ± 0.685	0.9617	0.10
		Salen + DMF		
288.15	229.78 ± 0.07	−8.7700 ± 0.598	0.9685	0.09
298.15	230.72 ± 0.07	−7.8834 ± 0.591	0.9622	0.09
308.15	231.75 ± 0.06	−7.0135 ± 0.498	0.9659	0.07
318.15	232.62 ± 0.06	−6.4010 ± 0.469	0.9638	0.07
		Salen + CH_2Cl_2		
283.15	223.77 ± 0.08	11.8181 ± 0.624	0.9773	0.09
288.15	223.92 ± 0.08	12.3678 ± 0.395	0.9798	0.10
293.15	224.03 ± 0.10	13.2482 ± 0.873	0.9705	0.13
298.15	224.32 ± 0.10	13.8656 ± 0.751	0.9799	0.12
		Salen + $CHCl_3$		
283.15	222.81 ± 0.05	4.8986 ± 0.483	0.9364	0.08
288.15	223.14 ± 0.07	5.1277 ± 0.606	0.9109	0.10
293.15	223.29 ± 0.08	6.6028 ± 0.736	0.9200	0.12
298.15	223.39 ± 0.11	8.6933 ± 1.023	0.9116	0.17

Table 4. Partial Molar Expansivities, E^0_ϕ, and Thermal Expansion Coefficients, α* of Salen in Organic Solvents at Different Temperatures

	$10^6\cdot E^0_\phi$/m^3·mol^{-1}·K^{-1}			
system	T/K = 288.15	T/K = 298.15	T/K = 308.15	T/K = 318.15
salen + DMSO	0.1174	0.1179	0.1184	0.1189
salen + DMA	0.0793	0.0803	0.0813	0.0823
salen + DMF	0.0532	0.0597	0.0662	0.0727
	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15
salen + CH_2Cl_2	0.0210	0.0310	0.0410	0.0510
salen + $CHCl_3$	0.0198	0.0218	0.0238	0.0258
	$10^6\cdot\alpha^*$ (K^{-1})			
	T/K = 288.15	T/K = 298.15	T/K = 308.15	T/K = 318.15
DMSO	1.1182	1.1271	1.1359	1.1447
DMA	0.6934	0.6792	0.6646	0.6501
DMF	1.1182	1.1271	1.1359	1.1447
	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15
CH_2Cl_2	−0.0483	−0.0726	−0.0969	−0.1210
$CHCl_3$	0.8095	0.8050	0.8003	0.7958

interactions dominate over solute−solute interactions in all of the solutions and experimental temperatures. It can be also seen that the standard partial molar volumes for salen decreased in the order V^0_ϕ(DMSO) > V^0_ϕ(DMA) > V^0_ϕ(DMF) > V^0_ϕ(CH_2Cl_2) > V^0_ϕ(CH_3Cl). Therefore, the values of standard partial molar volume increase with increasing polarity of the solvent due to the stronger solvation of the salen by higher polarity of the solvent. The positive values of V^0_ϕ for salen in the organic solvents studied indicate strong solute−solvent interactions. These interactions are strengthened with increasing temperature.

The S_v values are negative for DMSO, DMF, and DMF at all experimental temperatures and increase with increasing temperature. This means that in noninfinite dilute mixtures solute−solute interactions, apart from solute−solvent and solvent−solvent interactions, will be present and increase with increasing temperature. The positive values of S_v for salen in CH_3Cl and CH_2Cl_2 are, as a consequence of the dominance of attractive solute−solute interactions, short-range interactions over the solute−solvent interactions.[29]

The temperature dependence of V^0_ϕ can be expressed as,[25]

$$V^0_\phi = A + BT + CT^2 \qquad (3)$$

where A, B, and C are empirical parameters and T is the absolute temperature. The values of A, B, and C in eq 3 were obtained by the least-squares method. The calculated correlation coefficients of this equation for DMSO, DMF, DMA, CH_2Cl_2, and $CHCl_3$ are 0.99996, 0.99997, 0.99999, 0.99697, and 0.98906, respectively.

The partial molar expansivity E^0_ϕ was calculated by differentiating eq 3 with respect to temperature:

$$E^0_\phi = (\partial V^0_\phi/\partial T)_p = B + 2CT \qquad (4)$$

The calculated values of E^0_ϕ are given in Table 4. The E^0_ϕ values provide an important indicator of solute−solvent interactions and solvation properties. These values are also employed in interpreting of the structure-making or -breaking properties of various solutes.[30] The positive E^0_ϕ values indicate that the salen are kosmotropes (structure maker) in all studied organic solvents. This table also shows that E^0_ϕ values increase with increasing temperature. This may be ascribed to presence of caging effect. The E_ϕ^0 is a linear function of temperature. According to Hepler's equation[31]

$$T(\partial^2 V_\phi^0/\partial T^2)_p = -(\partial C_p/\partial P)_T \tag{5}$$

The sign of Hepler's constant $(\partial^2 V_\phi^0/\partial T^2)_p$ is a better criterion in characterizing the long-range structure-making and -breaking ability of the solute in the solution. If Hepler's constant is positive or very small and negative, the solute is a structure maker, and if its sign is negative, it is a structure breaker. The values of Hepler's constant are $-6.136 \cdot 10^{-5}$, $-1.202 \cdot 10^{-4}$, $3.25 \cdot 10^{-4}$, $5.573 \cdot 10^{-5}$, and $8.175 \cdot 10^{-5}$ for DMSO, DMF, CH_2Cl_2, $CHCl_3$, and DMA, respectively. The positive and small negative values of Hepler's constants for salen show that salen predominantly acts as a structure maker.

The results for the standard partial molar volumes were used for the calculation of the isobaric thermal expansion coefficient, α^*, of a solute defined as,[29]

$$\alpha^* = \frac{1}{V_\phi^0}\left(\frac{\partial V_\phi^0}{\partial T}\right)_p \tag{6}$$

The values of α^* are listed in Table 4. The highest value of α^* is obtained for DMSO and the lowest for CH_2Cl_2.

Conclusions

Densities of binary mixtures containing salen in several organic solvents have been measured at different temperatures. The apparent molar volume, V_ϕ, standard partial molar volume, V_ϕ^0, partial molar expansivity, E_ϕ^0, and isobaric thermal coefficient have been computed from the experimental density data. The values of V_ϕ^0 are positive for salen in organic solvents studied at all experimental temperatures and increase with increasing temperature. The values of standard partial molar volumes indicate the presence of strong solute−solvent interactions and are strengthened at higher temperatures. The standard partial molar volumes indicate that $V_\phi^0(\text{DMSO}) > V_\phi^0(\text{DMA}) > V_\phi^0(\text{DMF}) > V_\phi^0(CH_2Cl_2) > V_\phi^0(CH_3Cl)$. The E_ϕ^0 and the Hepler's constant values were found to be positive or very small and negative, which indicates that the salen Schiff base is predominately a structure maker in all studied organic solvents.

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