JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Partial Molar Volumes and Viscosity *B*-Coefficients of *N*,*N*′-Ethylene-bis(salicylideneiminato)cobalt(II) in Binary Mixtures of 1,4-Dioxane + Methanol at *T* = (298.15, 303.15, 308.15, and 313.15) K

Dhiraj Brahman and Biswajit Sinha*

Department of Chemistry, University of North Bengal, Darjeeling 734013, India

ABSTRACT: Partial molar volumes φ_V^0 and viscosity *B*-coefficients of *N*,*N*′-ethylene-bis(salicylideneiminato)cobalt(II), abbreviated as Co(salen), in different mass fractions (0 to 0.40) of 1,4-dioxane + methanol mixtures were determined from solution density and viscosity measurements at (298.15, 303.15, 308.15, and 313.15) K under ambient pressure. Apparent molar volumes φ_V and density data at the experimental temperatures were used to calculate the apparent molar expansibilities φ_E of Co(salen) solutions; the partial molar expansibilities φ_E^0 were then determined from the relation: $\varphi_E = \varphi_E^0 + S_E(m)^{1/2}$. The temperature dependence of φ_E^0 values yielded $(\partial\varphi_E^0/\partial T)_P$; the signs of the $(\partial\varphi_E^0/\partial T)_P$ values were discussed to reveal the structure promoting ability of Co(salen) in the experimental solvent/solvent mixtures. The activation parameters of viscous flow for the ternary solutions were also derived and discussed in terms of transition state theory. Various results indicated that the ternary system under investigation is characterized by structural changes and strong solute−solvent interactions.

INTRODUCTION

Mixed solvents are characterized by the variation of properties such as dielectric constant or viscosity, and so forth, enabling better studies on solute−solute and solute−solvent interactions. Furthermore, different properties strongly influenced by solvent properties can be derived in terms of concentration dependence of a solute. Alcohols in nonpolar solvents associate by means of hydrogen bonds into a series of *n*-mers.[1,2] In dilute solutions the predominant species are the unassociated molecules, while in concentrated solutions both linear and *n*-mers coexist. In solvents such as 1,4-dioxane that can form hydrogen bonds with methanol, the self-association of alcohols may be reduced/perturbed in favor of hydrogen-bonded structures when mixed together, leading to intermolecular association between methanol and 1,4-dioxane molecules.[3] Papanastasiou et al.[4] suggested that the binary mixtures of 1,4-dioxane and methanol are characterized by the formation of two intermolecular complexes (1,4-dioxane/methanol) of the types 1:1 and 1:2 and that 1,4-dioxane can associate through hydrogen bonds by either of its two oxygen atoms.

It is well-known that naturally occurring oxygen carriers and storage proteins contain transition metal ions to reversibly bind dioxygen. Since cobalt-Schiff base complexes were reported to be synthetic reversible oxygen carriers by Tsumaki,[5,6] many investigators have conducted extensive studies on the oxygen-carrying property of these complexes.[7−11] Among the cobalt-Schiff base complexes, the best known is *N*,*N*′-ethylene-bis(salicylideneiminato)-cobalt(II), abbreviated as Co(salen), which has a low-spin configuration with a square planar donor atom (ONNO) symmetry, and it can exist in different crystalline forms depending on the solvent used in its preparation. These crystalline forms have varying capacity for oxygenation in the solid state, and only a few solvents that can promote the oxygenation of Co(salen) were found to be ligated to the cobalt in the final oxygenated inactive form.[12] Hence solvent composition has a major role to play.

Ochiai et al.[13,14] indicated that oxygenation of the Co(II)L complex (where L is a solvent base ligand) forms either O_2/CoL (1:1 adduct) or LCo/O_2/CoL (2:1 adduct) and the 2:1 adduct is thermodynamically favored. Hence the solution behavior of Co(salen) in mixed solvent media like 1,4-dioxane + methanol will be quite intriguing and interesting. However, such studies on the solute−solute and solute−solvent interactions prevailing in solutions of Co(salen) in various pure and mixed solvents are rare in the literature. Again partial molar volumes φ_V^0 and viscosity *B*- coefficients in the solution phase provide valuable information about solute−solvent and solvent−solvent interactions[15−17] and thus are of fundamental importance for a proper understanding of the solution behavior of the solute under investigation. Hence in this paper an attempt has been undertaken to reveal the various interactions prevailing in the ternary mixtures of Co(salen) + 1,4-dioxane + methanol at (298.15, 303.15, 308.15, and 313.15) K under ambient pressure.

EXPERIMENTAL SECTION

Chemicals. Analytical reagent (AR) grade cobalt acetate, $Co(OAc)_2 \cdot 4H_2O$, 1,2-ethylenediamine, and salicylaldehyde, each of purity > 99 %, were procured from Thomas Baker, India. These chemicals were used without further purification. Spectroscopic grade methanol and 1,4-dioxane were procured from Merck, India and used as received. Both of these liquids have a purity (minimum assay, GC) > 99.8 % with 0.05 % of water. The various binary solvent mixtures were prepared by mass, and necessary adjustments were done to achieve exact mass fraction (w_1 = 0.10, 0.20, 0.30, and 0.40) of 1,4-dioxane in the binary solvent mixtures with methanol at 298.15 K. The physical

Received: February 10, 2011
Accepted: June 7, 2011
Published: June 17, 2011

dx.doi.org/10.1021/je200145r | *J. Chem. Eng. Data* 2011, 56, 3073–3082

Table 1. Density ρ and Viscosity η for Different Mixtures of 1,4-Dioxane (1) + Methanol (2) at T = (298.15 to 313.15) K

solvent mixture	T/K	$\rho\cdot10^{-3}$/kg·cm^{-3}		η/mPa·s	
		expt.	lit.	expt.	lit.
$w_1 = 0.00$	298.15	0.7866	0.78645[4]	0.547	0.542[4]
	303.15	0.7818	0.7819[18]	0.508	0.510[18]
	308.15	0.7769	0.77710[4]	0.471	0.469[4]
	313.15	0.7728	0.7720[19]	0.449	0.4470[19]
$w_1 = 0.10$	298.15	0.8112	0.8068[a]	0.550	0.544[a]
	303.15	0.8064	0.8005[a]	0.511	0.505[a]
	308.15	0.8017	0.7975[a]	0.473	0.472[a]
	313.15	0.7969	0.7365[a]	0.432	0.429[a]
$w_1 = 0.20$	298.15	0.8344	0.8278[a]	0.554	0.554[a]
	303.15	0.8288	0.8217[a]	0.517	0.514[a]
	308.15	0.8234	0.8184[a]	0.482	0.479[a]
	313.15	0.8184	0.7663[a]	0.448	0.436[a]
$w_1 = 0.30$	298.15	0.8525	0.8497[a]	0.565	0.568[a]
	303.15	0.8474	0.8438[a]	0.527	0.526[a]
	308.15	0.8426	0.8402[a]	0.489	0.491[a]
	313.15	0.8380	0.7973[a]	0.452	0.447[a]
$w_1 = 0.40$	298.15	0.8751		0.587	
	303.15	0.8702		0.548	
	308.15	0.8655		0.508	
	313.15	0.8606		0.467	
$w_1 = 1.00$	298.15	1.0273	1.0278[20]	1.196	1.196[20]
	303.15	1.0223	1.0222[21]	1.093	1.0937[21]
	308.15	1.0178	1.01689[4]	1.011	1.0112[4]
	313.15	1.0143	1.0144[22]	0.978	0.9785[22]

[a] Least-squared fitted values of density and viscosity data from ref 4.

properties of these solvent mixtures as given in Table 1 showed that the experimental densities and viscosities were more or less comparable to the values obtained by the least-squares fitting of the literature data[4] with necessary conversion of mole fractions into mass fractions or vice versa up to 308.15 K. A comparison of literature data[4,18−22] for the densities and viscosities of the pure liquids was also made in Table 1 with the experimentally determined values whenever available.

Co(salen) was prepared by a slight modification of a known method[5,23] from equimolar quantities of cobalt acetate and the Schiff base, SalenH$_2$, in methanol. The red crystalline precipitate of the cobalt complex was filtered off, washed, and dried in vacuo at room temperature for about (6 to 8 h) (84 % yield). The product was recrystallized from methanol. The purity of the complex was checked by elemental analysis (found: C, 59.10; H, 4.33; N, 8.63; O, 10.01.; Co, 18.11; calc: C, 59.09; H, 4.34; N, 8.61; O, 9.84; Co, 18.12) and IR spectroscopy. Elemental microanalyses were done by a Perkin-Elmer (model 240C) analyzer. The IR spectrum was recorded on Jasco 5300 FT-IR spectrophotometer. Characteristic IR bands for the prepared complex (Nujol, cm^{-1}) are: 1626.80 (1623.86[24]) for $\nu_{C=N}$, 1332.44 (1332.44[24]) for $\nu_{C=O}$, 430.70 (430.70[24]) for ν_{Co-O}, and 468.32 (468.32[24]) for ν_{Co-N}. The magnetic moment, measured with a Sherwood scientific magnetic balance, was found to be 2.71 μ_B (2.75 μ_B[24]) at room temperature. The molecular structures of the ligand, SalenH$_2$, and the complex, Co(salen), were depicted in Figure 1.

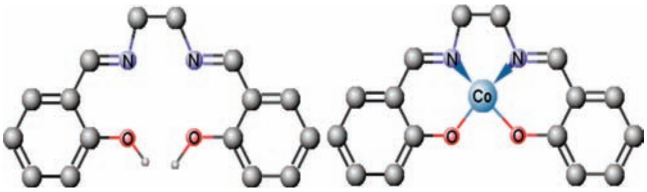

Figure 1. Molecular structure of SalenH$_2$ and Co(salen).

Before use Co(salen) was kept in a vacuum desiccator over anhydrous CaCl$_2$ for several hours. Then stock solutions of Co(salen) in different solvent mixtures (w_1 = 0.00, 0.10, 0.20, 0.30, and 0.40) were prepared by mass, and the working solutions were prepared by mass dilution. The mass measurements accurate to ± 0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The conversion of molality into molarity was accomplished using experimental density values. All solutions were prepared afresh before use. The uncertainty in molarity of the Co(salen) solutions was evaluated to ± 0.0001 mol·dm^{-3}.

Measurements. The densities were measured with a vibrating-tube density meter (Anton Paar, DMA 4500M), maintained at ± 0.01 K of the desired temperatures and calibrated at the experimental temperatures with doubly distilled water and dry air. The uncertainty in density was estimated to be ± 0.0001 g·cm^{-3}, and that of the temperature was ± 0.01 K.

The viscosity was measured by means of a suspended Ubbelohde type viscometer thoroughly cleaned, dried, and calibrated at the experimental temperatures with triply distilled water and purified methanol.[25−27] It was filled with experimental liquid and placed vertically in a glass-sided thermostat maintained constant to ± 0.01 K. After attainment of thermal equilibrium, the efflux times of flow of liquids were recorded with a digital stopwatch correct to ± 0.01 s. In all determinations, an average of triplicate measurements was taken into account, and adequate precautions were taken to minimize evaporation loses during the actual measurements. The uncertainty in viscosity measurements was within ± 0.003 mPa·s. Details of density and viscosity measurement methods and techniques have been described elsewhere.[28−30]

The absorption spectra of Co(salen) in different mixtures of 1,4-dioxane and methanol at a concentration of 5.0·10^{-5} mol·dm^{-3} were recorded on Shimatzu (Japan) double-beam UV−vis spectrophotometer (model UV-240) coupled with thermostatic arrangement (model TB-85) at ambient temperature using a quartz cell of 1 cm path length and spectroscopic grade methanol as the reference solvent.

RESULTS AND DISCUSSION

The experimental values of molalities m, densities ρ, viscosities η, and derived parameters for the experimental solutions of Co(salen) in different mass fractions of 1,4-dioxane + methanol mixtures at various temperatures are reported in Table 2. For the analysis of solvation state of a solute in solution phase and its interaction with solvent components, data of partial molar volumes are important. For this purpose, the apparent molar volumes φ_V were determined from the solution densities using the following relation:

$$\varphi_V = \frac{M}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0} \qquad (1)$$

where M is the molar mass of Co(salen), m is the molality of the solution, and ρ_0 and ρ are the densities of the solvent and solution,

Table 2. Molalities m, Densities ρ, Viscosities η, Apparent Molar Volumes φ_V, and $(\eta_r - 1)/(c)^{1/2}$ for Co(salen) in Different Mixtures of 1,4-Dioxane (1) + Methanol (2) at T = (298.15 to 313.15) K

m	$\rho\cdot 10^{-3}$	η	$\varphi_V\cdot 10^6$	$(\eta_r - 1)/(c)^{1/2}$
$\text{mol}\cdot\text{kg}^{-1}$	$\text{kg}\cdot\text{m}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{mol}^{-1/2}\cdot\text{dm}^{3/2}$
$w_1 = 0.00$				
T/K = 298.15				
0.0036	0.7871	0.551	188.92	0.1382
0.0046	0.7873	0.555	167.42	0.2438
0.0061	0.7876	0.561	148.38	0.3693
0.0087	0.7882	0.572	116.05	0.5540
0.0107	0.7886	0.582	111.14	0.6978
0.0127	0.7890	0.593	107.76	0.8410
T/K = 303.15				
0.0036	0.7823	0.512	188.69	0.1488
0.0046	0.7825	0.516	166.93	0.2625
0.0061	0.7828	0.521	147.65	0.3693
0.0087	0.7834	0.533	114.93	0.5965
0.0107	0.7838	0.540	109.96	0.6869
0.0127	0.7842	0.552	106.54	0.8705
T/K = 308.15 K				
0.0036	0.7774	0.473	188.44	0.0803
0.0046	0.7776	0.478	166.40	0.2477
0.0061	0.7779	0.483	146.88	0.3714
0.0087	0.7785	0.495	113.74	0.6176
0.0107	0.7789	0.502	108.71	0.7225
0.0127	0.7793	0.515	105.25	0.9389
T/K = 313.15				
0.0036	0.7733	0.453	188.22	0.1684
0.0046	0.7735	0.457	165.94	0.2970
0.0061	0.7738	0.463	146.21	0.4545
0.0087	0.7744	0.474	112.72	0.6798
0.0107	0.7748	0.481	107.64	0.7823
0.0127	0.7752	0.494	104.15	1.0124
$w_1 = 0.10$				
T/K = 298.15				
0.0035	0.8117	0.556	183.77	0.2062
0.0044	0.8119	0.559	162.53	0.2727
0.0059	0.8122	0.565	140.40	0.3935
0.0084	0.8128	0.575	113.83	0.5510
0.0104	0.8132	0.585	108.46	0.6940
0.0123	0.8136	0.594	104.15	0.8000
T/K = 303.15				
0.0035	0.8069	0.516	183.56	0.1850
0.0044	0.8071	0.520	158.57	0.2975
0.0059	0.8074	0.526	142.54	0.4236
0.0084	0.8080	0.536	110.23	0.5930
0.0104	0.8084	0.545	107.36	0.7256
0.0123	0.8088	0.556	102.99	0.8851
T/K = 308.15				
0.0035	0.8022	0.478	183.34	0.1998
0.0044	0.8024	0.482	158.06	0.3214
0.0059	0.8027	0.487	141.84	0.4315
0.0084	0.8033	0.497	109.15	0.6195
0.0104	0.8037	0.505	106.25	0.7426
0.0123	0.8041	0.516	101.83	0.9183
T/K = 313.15				
0.0035	0.7974	0.437	183.10	0.2188
0.0044	0.7976	0.441	157.51	0.3519
0.0059	0.7979	0.447	141.10	0.5062
0.0084	0.7985	0.457	108.01	0.7066
0.0104	0.7989	0.464	105.08	0.8131
0.0123	0.7993	0.475	100.61	1.0054
$w_1 = 0.20$				
T/K = 298.15				
0.0034	0.8349	0.558	178.49	0.1365
0.0043	0.8351	0.562	155.87	0.2407
0.0058	0.8354	0.568	142.01	0.3647
0.0082	0.8360	0.576	109.36	0.4813
0.0101	0.8364	0.586	105.15	0.6299
0.0120	0.8368	0.593	102.27	0.7040
T/K = 303.15				
0.0034	0.8293	0.521	178.26	0.1463
0.0043	0.8295	0.525	155.34	0.2579
0.0058	0.8298	0.531	141.29	0.3908
0.0082	0.8304	0.541	108.19	0.5627
0.0101	0.8308	0.549	103.93	0.6750
0.0120	0.8312	0.555	101.01	0.7387
T/K = 308.15				
0.0034	0.8239	0.487	178.02	0.1961
0.0043	0.8241	0.491	156.85	0.3154
0.0058	0.8244	0.497	140.56	0.4491
0.0082	0.8250	0.505	107.03	0.5826
0.0101	0.8254	0.513	102.71	0.7060
0.0120	0.8258	0.521	99.75	0.8132
T/K = 313.15				
0.0034	0.8189	0.453	177.77	0.2110
0.0043	0.8191	0.457	155.99	0.3393
0.0058	0.8194	0.464	139.86	0.5206
0.0082	0.8200	0.471	105.92	0.6269
0.0101	0.8204	0.479	101.55	0.7596
0.0120	0.8208	0.487	98.55	0.8793
$w_1 = 0.30$				
T/K = 298.15				
0.0033	0.8530	0.569	172.96	0.1338
0.0042	0.8532	0.573	152.09	0.2360
0.0056	0.8535	0.578	135.68	0.3320
0.0080	0.8541	0.587	106.15	0.4720
0.0099	0.8545	0.595	103.33	0.5790
0.0117	0.8549	0.603	99.02	0.6726
T/K = 303.15				
0.0033	0.8479	0.531	172.74	0.1435
0.0042	0.8481	0.535	151.62	0.2530
0.0056	0.8484	0.541	135.01	0.3873
0.0080	0.8490	0.549	105.13	0.5060
0.0099	0.8494	0.557	102.27	0.6208
0.0117	0.8498	0.566	97.91	0.7438
T/K = 308.15				
0.0033	0.8431	0.494	172.52	0.1933
0.0042	0.8433	0.498	151.15	0.3109
0.0056	0.8436	0.504	134.35	0.4472
0.0080	0.8442	0.513	104.13	0.5993
0.0099	0.8446	0.521	101.24	0.7183
0.0117	0.8450	0.528	96.83	0.8056
T/K = 313.15				
0.0033	0.8385	0.456	172.29	0.1673
0.0042	0.8387	0.461	150.69	0.3363
0.0056	0.8390	0.468	133.70	0.5160
0.0080	0.8396	0.476	103.15	0.6483
0.0099	0.8400	0.484	100.23	0.7771
0.0117	0.8404	0.491	95.77	0.8715

Table 2. Continued

m	$\rho \cdot 10^{-3}$	η	$\varphi_V \cdot 10^6$	$(\eta_r - 1)/(c)^{1/2}$
$\text{mol} \cdot \text{kg}^{-1}$	$\text{kg} \cdot \text{m}^{-3}$	$\text{mPa} \cdot \text{s}$	$\text{m}^3 \cdot \text{mol}^{-1}$	$\text{mol}^{-1/2} \cdot \text{dm}^{3/2}$
		$w_1 = 0.40$		
		$T/\text{K} = 298.15$		
0.0032	0.8756	0.591	167.56	0.1288
0.0041	0.8758	0.594	148.63	0.1988
0.0055	0.8761	0.598	134.12	0.2704
0.0078	0.8767	0.607	103.64	0.4130
0.0096	0.8771	0.612	99.42	0.4644
0.0114	0.8775	0.621	96.52	0.5792
		$T/\text{K} = 303.15$		
0.0032	0.8707	0.551	167.35	0.1035
0.0041	0.8709	0.555	148.20	0.2129
0.0055	0.8712	0.561	133.53	0.3423
0.0078	0.8718	0.567	102.71	0.4203
0.0096	0.8722	0.575	98.44	0.5408
0.0114	0.8726	0.582	95.51	0.6236
		$T/\text{K} = 308.15$		
0.0032	0.8660	0.514	167.13	0.2233
0.0041	0.8662	0.518	147.77	0.3325
0.0055	0.8665	0.524	132.94	0.4545
0.0078	0.8671	0.532	101.79	0.5769
0.0096	0.8675	0.540	97.48	0.6915
0.0114	0.8679	0.546	94.51	0.7518
		$T/\text{K} = 313.15$		
0.0032	0.8611	0.472	166.89	0.2024
0.0041	0.8613	0.476	147.31	0.3255
0.0055	0.8616	0.481	132.31	0.4370
0.0078	0.8622	0.491	100.81	0.6275
0.0096	0.8626	0.497	96.44	0.7052
0.0114	0.8630	0.503	93.44	0.7787

respectively. Uncertainties in φ_V values were within the range $(0.02 \text{ to } 0.05) \cdot 10^{-6}\ \text{m}^3 \cdot \text{mol}^{-1}$. As the plots of φ_V against square root of molar concentration $(m)^{1/2}$ were not linear, φ_V values were fitted to the following equation:[31]

$$\varphi_V = \varphi_V^0 + A_V\sqrt{m} + B_V m \tag{2}$$

where φ_V^0 is the partial molar volume at infinite dilution, and A_V and B_V are two adjustable parameters. The φ_V^0 values were determined by fitting the dilute data $(m < 0.1)$ to eq 2 using a least-squares

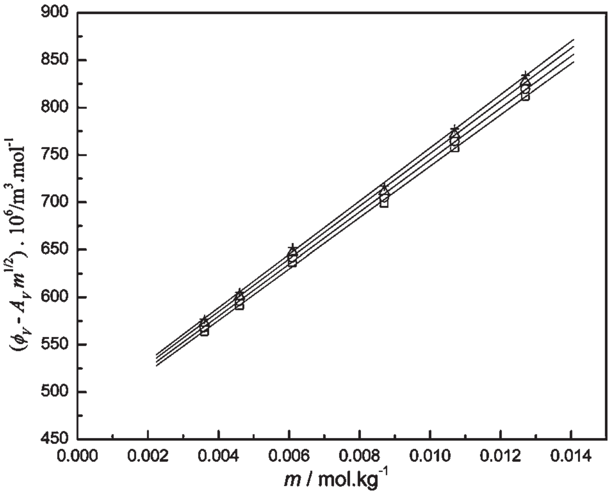

Figure 2. Variation of the parameter $(\varphi_V - A_V(m)^{1/2})$ as a function of molality (m) of Co(salen) in methanol at T = (298.15 to 313.15) K: □, 298.15 K; ○, 303.15 K; △, 308.15 K; and +, 313.15 K.

Table 3. Partial Molar Volumes ϕ_V^0 and Adjustable Parameters A_V and B_V for Co(salen) in Different Mixtures of 1,4-Dioxane (1) + Methanol (2) with Standard Deviations σ at T = (298.15 to 313.15) K[a]

T	$\varphi_V^0 \cdot 10^6$	$A_V \cdot 10^6$	$B_V \cdot 10^6$	$\sigma \cdot 10^6$
K	$\text{m}^3 \cdot \text{mol}^{-1}$	$\text{m}^3 \cdot \text{mol}^{-1.5}$	$\text{m}^3 \cdot \text{mol}^{-2}$	$\text{m}^3 \cdot \text{mol}^{-1}$
		$w_1 = 0.00$		
298.15	467.11 (± 0.02)	−6248.36 (± 2.18)	27089.97 (± 2.06)	0.33
303.15	470.30 (± 0.02)	−6325.42 (± 2.02)	27425.22 (± 2.09)	0.34
308.15	473.66 (± 0.02)	−6406.48 (± 2.20)	27778.05 (± 2.10)	0.35
313.15	476.56 (± 0.02)	−6476.98 (± 2.14)	28087.82 (± 2.17)	0.36
		$w_1 = 0.10$		
298.15	466.58 (± 0.03)	−6518.85 (± 0.16)	29348.60 (± 1.67)	0.11
303.15	467.72 (± 0.03)	−6571.78 (± 0.45)	29618.04 (± 1.83)	0.02
308.15	470.85 (± 0.03)	−6649.28 (± 0.49)	29968.32 (± 1.81)	0.02
313.15	474.12 (± 0.03)	−6730.53 (± 0.60)	30336.27 (± 1.90)	0.02
		$w_1 = 0.20$		
298.15	431.38 (± 0.06)	−5854.27 (± 1.24)	25934.18 (± 3.61)	0.55
303.15	434.59 (± 0.06)	−5933.79 (± 1.34)	26286.64 (± 3.67)	0.56
308.15	439.20 (± 0.06)	−6020.67 (± 1.96)	26576.76 (± 3.85)	0.76
313.15	441.83 (± 0.06)	−6091.25 (± 1.96)	26903.17 (± 3.87)	0.75
		$w_1 = 0.30$		
298.15	425.81(± 0.12)	−5965.73 (± 1.01)	27221.04 (± 11.45)	0.01
303.15	428.62 (± 0.12)	−6037.18 (± 0.98)	27546.49 (± 11.59)	0.01
308.15	431.38 (± 0.12)	−6107.75 (± 1.17)	27870.69 (± 11.70)	0.01
313.15	433.99 (± 0.13)	−6174.86 (± 1.01)	28177.05 (± 11.87)	0.01
		$w_1 = 0.40$		
298.15	396.00 (± 0.03)	−5387.12 (± 3.07)	24085.03 (± 2.01)	0.75
303.15	398.38 (± 0.03)	−5448.31 (± 3.15)	24359.82 (± 2.01)	0.77
308.15	400.66 (± 0.03)	−5507.29 (± 2.98)	24623.87 (± 2.03)	0.77
313.15	403.06 (± 0.03)	−5569.35 (± 3.11)	24899.72 (± 2.07)	0.80

[a] Standard errors are given in the parentheses.

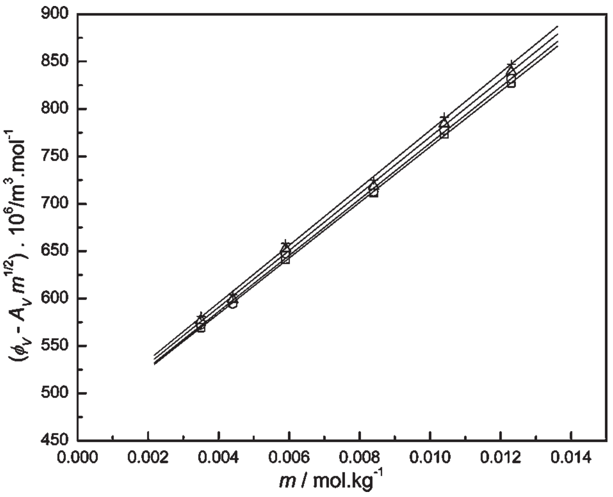

Figure 3. Variation of the parameter $(\varphi_V - A_V(m)^{1/2})$ as a function of molality (m) of Co(salen) in the 1,4-dioxane (1) + methanol (2) mixture with $w_1 = 0.10$ at $T = (298.15$ to $313.15)$ K: □, 298.15 K; ○, 303.15 K; △, 308.15 K; and +, 313.15 K.

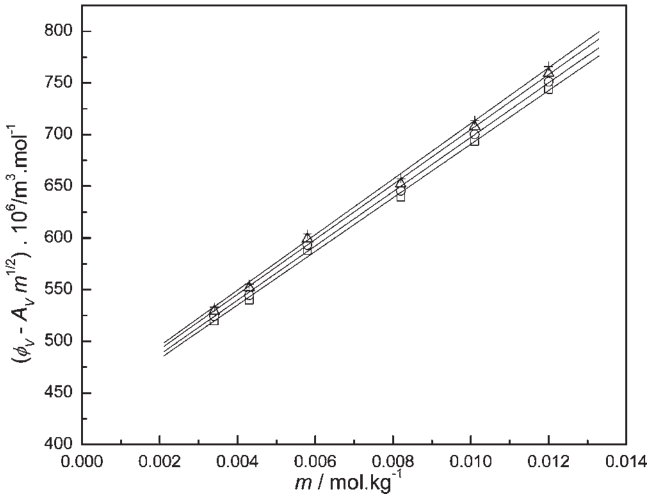

Figure 4. Variation of the parameter $(\varphi_V - A_V(m)^{1/2})$ as a function of molality (m) of Co(salen) in the 1,4-dioxane (1) + methanol (2) mixture with $w_1 = 0.20$ at $T = (298.15$ to $313.15)$ K: □, 298.15 K; ○, 303.15 K; △, 308.15 K; and +, 313.15 K.

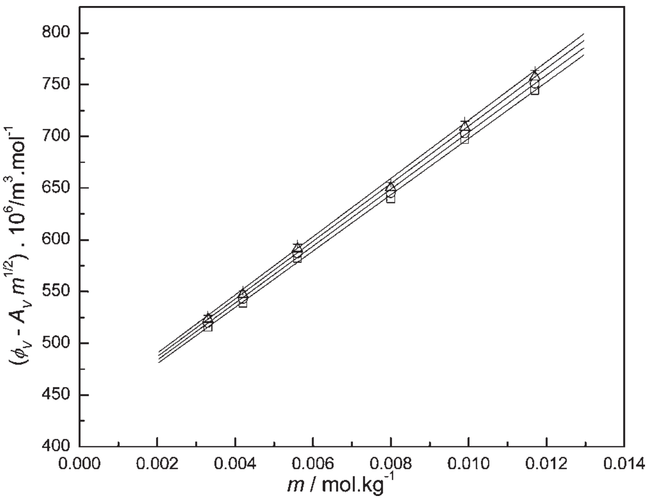

Figure 5. Variation of the parameter $(\varphi_V - A_V(m)^{1/2})$ as a function of molality (m) of Co(salen) in the 1,4-dioxane (1) + methanol (2) mixture with $w_1 = 0.30$ at $T = (298.15$ to $313.15)$ K: □, 298.15 K; ○, 303.15 K; △, 308.15 K; and +, 313.15 K.

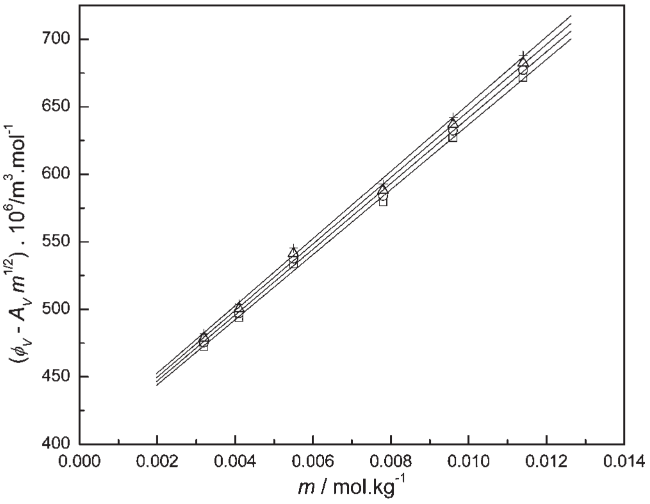

Figure 6. Variation of the parameter $(\varphi_V - A_V(m)^{1/2})$ as a function of molality (m) of Co(salen) in the 1,4-dioxane (1) + methanol (2) mixture with $w_1 = 0.40$ at $T = (298.15$ to $313.15)$ K: □, 298.15 K; ○, 303.15 K; △, 308.15 K; and +, 313.15 K.

regression method, and the coefficient of regression (R^2) values were within the range 0.9991 to 0.9999. The values of φ_V^0 at each temperature are reported in Table 3. The estimated uncertainties in φ_V^0 were equal to the standard deviation σ, the root-mean-square of the deviations between the experimental and the calculated φ_V values for each data point. φ_V^0 values were further optimized from the linear variation of the parameter $(\varphi_V - A_V(m)^{1/2})$ against the molalities (m) of the experimental solutions in different solvent systems at different experimental temperatures (Figures 2 to 6).

Table 3 shows that φ_V^0 values are positive and increase with a rise in the temperature but decrease as the amount of 1,4-dioxane in the mixtures increases. This indicates the presence of strong solute−solvent interactions ,and these interactions are further strengthened at higher temperatures but weakened with higher content of the cyclic diether. In this study, Co(salen) was actually taken in its oxygenated form and methanol being a protic solvent may interact with the dioxygen coordinated to sixth position of Co(salen), resulting in the rapid breakdown of the dioxygen complex with oxidation of Co(II) to Co(III). It may also interact with Co(salen) via hydrogen bond formation with ONNO sites of the complex. It is also reported that 1,4-dioxane forms extensive hydrogen bonding with methanol. Hence with increasing amount of 1,4-dioxane in the solvent mixtures, the interaction between methanol and Co(salen) decreases owing to favorable hydrogen-bond interaction between 1,4-dioxane and methanol molecules. Thus the addition of 1,4-dioxane decreases φ_V as well as φ_V^0 values for the ternary systems under investigation. A schematic representation of such probable molecular interactions has been depicted in Figure 7. Although φ_V values decrease slightly as the temperature increases, φ_V^0 values increase appreciably. This is probably due to greater solvation of Co(salen) with methanol and 1,4-dioxane molecules owing to more molecular

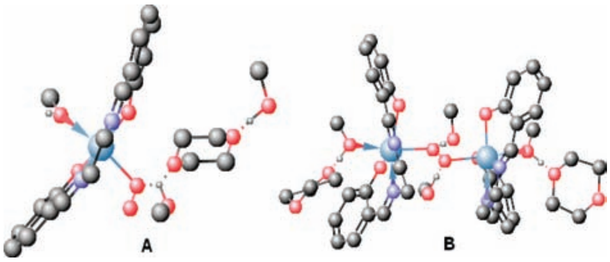

Figure 7. Schematic representation of different hydrogen-bond interactions in the ternary solutions of Co(salen) + 1,4-dioxane + methanol: A, interactions with the 1:1 oxygen adduct of Co(salen); B: interactions with the 2:1 oxygen adduct of Co(salen).

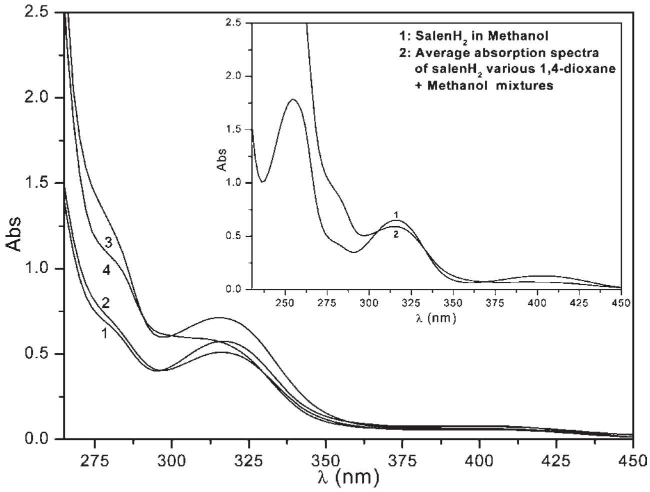

Figure 8. Changes in the UV−vis absorption spectra of SalenH$_2$ solutions in different 1,4-dioxane (1) + methanol (2) mixtures at 298.15 K: 1, in a mixture with w_1 = 0.10; 2, in a mixture with w_1 = 0.20; 3, in a mixture with w_1 = 0.30; 4, in a mixture with w_1 = 0.40. Inset: 1, SalenH$_2$ in methanol; 2, average absorption spectra in different 1,4-dioxane + methanol mixtures at 298.15 K.

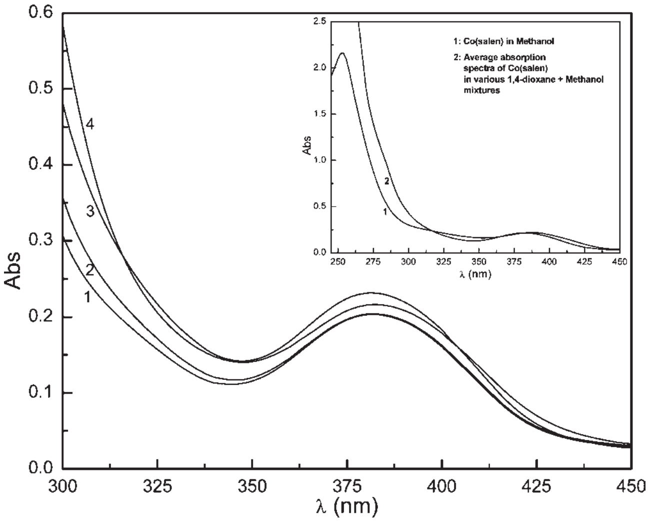

Figure 9. Changes in the UV−vis absorption spectra of Co(salen) solutions in different 1,4-dioxane (1) + methanol (2) mixtures at 298.15 K: 1, in a mixture with w_1 = 0.10; 2, in a mixture with w_1 = 0.20; 3, in a mixture with w_1 = 0.30; 4, in a mixture with w_1 = 0.40. Inset: 1, Co(salen) in methanol; 2, average absorption spectrum in different 1,4-dioxane + methanol mixtures at 298.15 K.

collisions at elevated temperatures; thus the effect of B_V predominates over A_V in characterizing resultant φ_V^0 values. Having two oxygen atoms in its structure 1,4-dioxane may form a 2:1 complex with Co(salen) like dioxygen, but our results indicate that such complex formation is hindered due to the bulkier size of 1,4-dioxane compared to methanol.

These results are also reflected in the UV−vis absorption spectra of the studied solutions. Figure 8 shows the absorption spectra of the Schiff base, SalenH$_2$ in methanol, and various mixed solvents at 298.15 K. The spectra in methanol are characterized by the presence of two strong peaks at (254 and 316) nm and a weak peak at 404 nm, assigned to $\pi \rightarrow \pi^*$ transitions, $n \rightarrow \pi^*$ transitions involving the molecular orbitals of $C=N^{\bullet\bullet}$ chromophore and benzene ring and $n \rightarrow \pi^*$ transitions of $C=N^{\bullet\bullet}$ chromophore, respectively. The appearance of the weak peak at 404 nm indicates that the keto−enol tautomeric equilibrium between an −OH (enol-imine) and −NH (keto-enamine) forms of the Schiff base[32] exists to some extent in methanol. But when 1,4-dioxane is introduced, the 404 nm peak gradually disappears and forms a valley as the concentration of 1,4-dioxane increases in the ternary solutions. Thus the position of the weak peak varies with the polarity of the solvent. Also the 316 nm peak suffers from hypochromic shifts on addition of 1,4-dioxane. The absorption spectra of Co(salen) in methanol and various mixed solvents at 298.15 K are depicted in Figure 9; it shows that the 404 nm peak of the Schiff base is blue-shifted to 388 nm in the methanol due to coordination to Co(II). In the mixed solvents this peak is further blue-shifted to 382 nm and suffers from hyperchromic shifts probably due to the decrease in polarity of the solvent mixture with a further addition of 1,4-dioxane.

Apparent molar volumes φ_V and density data at the experimental temperatures were used to calculate the apparent molar expansibilities φ_E of Co(salen) solutions using the relation:[33]

$$\varphi_E = \alpha\varphi_V + \frac{1000(\alpha - \alpha_0)}{m\rho_0} \tag{3}$$

where α and α_0 are the coefficients of isobaric thermal expansion of the solvent and solution, respectively, and other symbols have their usual significance. α and α_0 are defined as: $\alpha_0 = -\rho_0^{-1}(\partial\rho_0/\partial T)_P$ and $\alpha = -\rho^{-1}(\partial\rho/\partial T)_P$; the corresponding uncertainty was $\pm\, 5\cdot10^{-6}\ \mathrm{K}^{-1}$. The uncertainty in apparent molar expansibilities φ_E was within $\pm\, 0.001\cdot10^{-6}\ \mathrm{m^3\cdot mol^{-1}\cdot K^{-1}}$. The partial molar expansibilities φ_E^0 were then determined from the relation:[33]

$$\varphi_E = \varphi_E^0 + S_E\sqrt{m} \tag{4}$$

$(\partial\varphi_E^0/\partial T)_P$ values were obtained from the slope of a linear fit of φ_E^0 values against the experimental temperature T with the coefficient of regression (R^2) values within the range 0.9991 to 0.9999. The φ_E^0 values for different experimental solutions at different temperatures are given in Table 4. It reveals that φ_E^0 values are negative and further decrease gradually as the temperature increases for all of the solutions. This may be attributed to structural perturbation caused by the addition of the cyclic diether or to the appearance of caging/packing effect,[34,35] and Co(salen) seemed to behave more or less like common electrolytes[31] in binary mixtures of 1,4-dioxane with methanol. However, such a gradual decrease in φ_E^0 values with increasing temperature suggests a gradual disappearance of such effects

Table 4. Partial Molar Expansibilities ϕ_E^0 for Co(salen) in Different Mixtures of 1,4-Dioxane (1) + Methanol (2) at T = (298.15 to 313.15) K[a]

solvent mixture	$\varphi_E^0 \cdot 10^4$/m$^3\cdot$mol$^{-1}\cdot$K^{-1}				$S_E \cdot 10^4$/m$^3\cdot$mol$^{-1}\cdot$K^{-1}				$(\delta\varphi_E^0/\delta T)_P \cdot 10^6$
	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K	m$^3\cdot$mol$^{-1}\cdot$K^{-2}
w_1 = 0.00	−1.636 (±0.062)	−1.666 (±0.063)	−1.698 (±0.064)	−1.726 (±0.064)	−18.867 (±0.711)	−19.215 (±0.718)	−19.579 (±0.724)	−19.891 (±0.730)	−0.601 (±0.001)
w_1 = 0.10	−1.614 (±0.064)	−1.643 (±0.065)	−1.672 (±0.065)	−1.703 (±0.066)	−17.727 (±0.742)	−18.045 (±0.748)	−18.362 (±0.755)	−18.694 (±0.762)	−0.591 (±0.001)
w_1 = 0.20	−1.691 (±0.064)	−1.725 (±0.065)	−1.759 (±0.066)	−1.792 (±0.066)	−19.139 (±0.752)	−19.530 (±0.760)	−19.915 (±0.768)	−20.282 (±0.755)	−0.676 (±0.001)
w_1 = 0.30	−1.508 (±0.059)	−1.535 (±0.059)	−1.562 (±0.060)	−1.587 (±0.060)	−16.445 (±0.699)	−16.743 (±0.705)	−17.029 (±0.712)	−17.311 (±0.717)	−0.532 (±0.001)
w_1 = 0.40	−1.416 (±0.056)	−1.439 (±0.056)	−1.463 (±0.057)	−1.488 (±0.057)	−15.918 (±0.669)	−16.189 (±0.675)	−16.453 (±0.680)	−16.735 (±0.686)	−0.485 (±0.001)

[a] Standard errors are given in the parentheses.

leading to the release of CH_3OH molecules in favor of hydrogen bond interactions with 1,4-dioxane molecules and thus decreases volumes and increases densities of the solutions (Table 2). According to Hepler,[36] the sign of $(\delta\varphi_E^0/\delta T)_P$ is a better criterion in characterizing the long-range structure-making or -breaking ability of a solute in solution phase. If the term $(\delta\varphi_E^0/\delta T)_P$ is small negative or positive, the solute is a structure maker; otherwise it is a structure breaker. The $(\delta\varphi_E^0/\delta T)_P$ values for different ternary solutions are given in Table 4, and Co(salen) was found to act as a net structure promoter in the presence of 1,4-dioxane.

The viscosity data for the solutions of Co(salen) in different mass fractions (w_1 = 0.00, 0.10, 0.20, 0.30, and 0.40) of 1,4-dioxane + methanol mixtures were analyzed using the Jones−Dole equation:[37]

$$(\eta/\eta_0 - 1)\sqrt{c} = (\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \tag{5}$$

where $\eta_r = \eta/\eta_0$; η_0 and η are the viscosities of solvent and solution, respectively. A and B are the coefficients estimated by a least-squares regression method, and the coefficient of regression (R^2) values were within the range 0.9882 to 0.9993; these coefficients are reported in Table 5. The viscosity B-coefficient[38,39] reflects the effects of solute−solvent interactions on the solution viscosity similar to φ_V^0. Table 5 shows that the viscosity B-coefficients for Co(salen) in the studied solvent systems are positive, and the trend is in line with the φ_V^0 values supporting the results discussed earlier on the basis of φ_V^0 values. However, the A-coefficients are negative indicating the presence of weak solute−solute interactions in the ternary solutions and supports the results obtained on the basis of the viscosity B-coefficients for all of the studied solutions.

According to transition state theory of relative viscosity as suggested by Feakings et al.,[38] the free energy of activation of viscous flow per mole of the solute, $\Delta\mu_2^{0\neq}$, is related to the viscosity B-coefficients by the following relation:

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + RT(1000B + \varphi_{V,2}^0 - \varphi_{V,1}^0)/\varphi_{V,1}^0 \tag{6}$$

where $\varphi_{V,1}^0$ and $\varphi_{V,2}^0$ are the partial molar volumes of the solvent and solute, respectively. The free energy of activation of viscous flow for the solvent/solvent mixture per mole, $\Delta\mu_1^{0\neq}$, is given by the relation:[38,39]

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ \ln(\eta_0\varphi_{V,1}^0/hN_A) \tag{7}$$

where N_A is Avogadro's number and the other symbols have their usual significance. The entropy of activation for ternary solutions $\Delta S_2^{0\neq}$ was obtained from the negative slope of the plots of $\Delta\mu_2^{0\neq}$ against T,

$$\Delta S_2^{0\neq} = -d(\Delta\mu_2^{0\neq})/dT \tag{8}$$

and the activation enthalpy $(\Delta H_2^{0\neq})$ has been calculated using the relation,[38]

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \tag{9}$$

The parameters $(\varphi_{V,2}^0 - \varphi_{V,1}^0)$, $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $\Delta H_2^{0\neq}$, and $T\Delta S_2^{0\neq}$ are reported in Table 6. The values $\Delta\mu_2^{0\neq}$ contain the change in the free energy of activation of solvent molecules in presence of solute as well as the contribution from the movement of solute molecules. Table 6 shows that $\Delta\mu_1^{0\neq}$ is almost invariant of the solvent compositions and temperatures, implying that $\Delta\mu_2^{0\neq}$ is dependent mainly on the viscosity B-coefficients and $(\varphi_{V,2}^0 - \varphi_{V,1}^0)$ terms. $\Delta\mu_2^{0\neq}$ values were positive at all of the experimental temperatures suggesting that the process of viscous flow becomes difficult as the temperature increases but becomes easier to some

Table 5. Values of A and B-Coefficients for Co(salen) in Different Mixtures of 1,4-Dioxane (1) + Methanol (2) with Standard Deviations σ at T = (298.15 to 313.15) K[a]

	solvent mixtures			
viscosity coefficients	298.15 K	303.15 K	308.15 K	313.15 K
		$w_1 = 0.00$		
$A \cdot 10^6/\text{m}^{3/2}\cdot\text{mol}^{-1/2}$	−0.644 (±0.001)	−0.647 (± 0.001)	−0.827 (±0.001)	−0.752 (±0.001)
$B \cdot 10^6/\text{m}^{3}\cdot\text{mol}^{-1}$	14.702 (±0.012)	14.954 (±0.013)	17.471 (±0.002)	17.440 (±0.003)
$\sigma \cdot 10^6/\text{m}^{3/2}\cdot\text{mol}^{-1/2}$	0.001	0.004	0.003	0.001
		$w_1 = 0.10$		
$A \cdot 10^6/\text{m}^{3/2}\cdot\text{mol}^{-1/2}$	−0.486 (±0.001)	−0.569 (± 0.001)	−0.577 (±0.001)	−0.619 (±0.001)
$B \cdot 10^6/\text{m}^{3}\cdot\text{mol}^{-1}$	12.782 (±0.008)	14.341 (±0.006)	14.789 (±0.002)	16.163 (±0.004)
$\sigma \cdot 10^6/\text{m}^{3/2}\cdot\text{mol}^{-1/2}$	0.001	0.001	0.001	0.002
		$w_1 = 0.20$		
$A \cdot 10^6/\text{m}^{3/2}\cdot\text{mol}^{-1/2}$	−0.482 (±0.001)	−0.515 (± 0.001)	−0.458 (±0.006)	−0.480 (±0.001)
$B \cdot 10^6/\text{m}^{3}\cdot\text{mol}^{-1}$	11.944 (±0.008)	12.854 (±0.008)	12.801 (±0.002)	13.730 (±0.004)
$\sigma \cdot 10^6/\text{m}^{3/2}\cdot\text{mol}^{-1/2}$	0.001	0.001	0.001	0.001
		$w_1 = 0.30$		
$A \cdot 10^6/\text{m}^{3/2}\cdot\text{mol}^{-1/2}$	−0.448 (±0.001)	−0.487 (± 0.001)	−0.469 (±0.001)	−0.541 (±0.001)
$B \cdot 10^6/\text{m}^{3}\cdot\text{mol}^{-1}$	11.209 (±0.008)	12.249 (±0.005)	13.010 (±0.004)	14.509 (±0.005)
$\sigma \cdot 10^6/\text{m}^{3/2}\cdot\text{mol}^{-1/2}$	0.001	0.001	0.001	0.002
		$w_1 = 0.40$		
$A \cdot 10^6/\text{m}^{3/2}\cdot\text{mol}^{-1/2}$	−0.364 (±0.000)	−0.438 (± 0.001)	−0.343 (±0.001)	−0.422 (±0.001)
$B \cdot 10^6/\text{m}^{3}\cdot\text{mol}^{-1}$	9.282 (±0.006)	10.697 (±0.002)	11.214 (±0.003)	12.390 (±0.004)
$\sigma \cdot 10^6/\text{m}^{3/2}\cdot\text{mol}^{-1/2}$	0.001	0.001	0.002	0.003

[a] Standard errors are given in the parentheses.

Table 6. Values of $(\phi_{V,2}^{0} - \varphi_{V,1}^{0})$, $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $T\Delta S_2^{0\neq}$, and $\Delta H_2^{0\neq}$ for Co(salen) in Different Mixtures of 1,4-Dioxane (1) + Methanol (2) at T = (298.15 to 313.15) K

parameter	298.15 K	303.15 K	308.15 K	313.15 K
		$w_1 = 0.00$		
$(\varphi_{V,2}^{0} - \varphi_{V,1}^{0}) \cdot 10^6/\text{m}^3\cdot\text{mol}^{-1}$	426.38	429.32	432.42	435.10
$\Delta\mu_1^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	9.97	9.97	9.95	10.00
$\Delta\mu_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	931.72	955.97	1122.15	1132.50
$T\Delta S_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	−4582.62	−4659.47	−4736.32	−4813.17
$\Delta H_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	−3650.89	−3703.50	−3614.17	−3680.67
		$w_1 = 0.10$		
$(\varphi_{V,2}^{0} - \varphi_{V,1}^{0}) \cdot 10^6/\text{m}^3\cdot\text{mol}^{-1}$	424.39	425.28	428.16	431.17
$\Delta\mu_1^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	10.07	10.07	10.05	9.99
$\Delta\mu_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	786.10	887.09	923.40	1016.10
$T\Delta S_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	−4331.00	−4403.63	−4476.26	−4548.89
$\Delta H_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	−3544.90	−3516.54	−3552.86	−3532.79
		$w_1 = 0.20$		
$(\varphi_{V,2}^{0} - \varphi_{V,1}^{0}) \cdot 10^6/\text{m}^3\cdot\text{mol}^{-1}$	387.38	390.30	394.62	396.97
$\Delta\mu_1^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	10.19	10.21	10.21	10.20
$\Delta\mu_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	704.97	763.84	768.49	830.16
$T\Delta S_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	−2267.27	−2305.29	−2343.31	−2381.34
$\Delta H_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	−1562.30	−1541.45	−1574.82	−1551.17
		$w_1 = 0.30$		
$(\varphi_{V,2}^{0} - \varphi_{V,1}^{0}) \cdot 10^6/\text{m}^3\cdot\text{mol}^{-1}$	379.36	381.89	384.38	386.73
$\Delta\mu_1^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	10.38	10.39	10.38	10.36
$\Delta\mu_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	628.77	691.51	740.55	831.04
$T\Delta S_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	−3910.81	−3976.39	−4041.98	−4107.56
$\Delta H_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	−3282.04	−3284.88	−3301.43	−3276.52
		$w_1 = 0.40$		
$(\varphi_{V,2}^{0} - \varphi_{V,1}^{0}) \cdot 10^6/\text{m}^3\cdot\text{mol}^{-1}$	346.88	348.98	351.01	353.12
$\Delta\mu_1^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	10.61	10.63	10.62	10.59
$\Delta\mu_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	496.58	574.30	607.27	674.90
$T\Delta S_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	−3386.64	−3443.44	−3500.23	−3557.03
$\Delta H_2^{0\neq}/\text{kJ}\cdot\text{mol}^{-1}$	−2890.06	−2869.14	−2892.96	−2882.12

extent as the content of 1,4-dioxane in ternary solutions increases; that is, the formation of the transition state becomes less favorable as temperature increases but 1,4-dioxane favors its formation.[38] The quantity ($\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}$) is the change in the activation energy per mole of solute on replacing one mole of solvent by one mole of solute in an infinite dilution, and hence according to Feakings et al.[38] $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$, for solutes with positive viscosity *B*-coefficients, indicates stronger solute−solvent interactions, thereby suggesting the formation of transition state to be accompanied by the rupture and distortion of the intermolecular forces in solvent structure.[38] The greater the value of $\Delta\mu_2^{0\neq}$, the greater is the structure-promoting tendency of a solute, and the positive values of $\Delta\mu_2^{0\neq}$ for Co(salen) in the different ternary solutions suggest it to be a net structure promoter in the studied ternaries. The negative values of $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ for all the experimental solutions and temperatures suggest that the transition state is associated with bond formation and increase in order.

■ CONCLUSION

In summary, φ_V^0 and viscosity *B*-coefficient values for Co(salen) indicate the presence of strong solute−solvent interactions, and these interactions are further strengthened at higher temperatures but decrease for a higher content of 1,4-dioxane in the ternaries. Also, Co(salen) acts as a net methanol structure promoter in the ternary solutions.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +91 353 2776381; Fax: +91 353 2699001. E-mail: biswachem@gmail.com.

Funding Sources

The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. F540/27/DRS/2007, SAP-1) for financial support. One of the authors (D.B.) is also thankful to UGC, India for granting him a UGC BSR Research Fellowship in Science (Ref. No.: 4-1/2008 (BSR)).

■ REFERENCES

(1) Vinogradov, S. N. *Hydrogen Bonding*; Van Nostrand Reinhold: New York, 1971; pp 16 and 127.

(2) Kay, R. L.; Evans, D. F.; Matesich, M. A. *Solute-Solvent Interactions*; Marcel Dekker: New York, 1976; Vol. 2, p 133.

(3) Syrkin, Y. K.; Dyatkina, M. E. *Structure of Molecules and The Chemical Bond*, Dover: New York, 1964; p 127.

(4) Papanastasiou, G. E.; Zlogas, I. I. Physical Behavior of Some Reaction Media. 3. Density, Viscosity, Dielectric Constant, and Refractive Index Changes of Methanol + Dioxane Mixtures at Several Temperatures. *J. Chem. Eng. Data* **1992**, *37*, 167–172.

(5) Tsumaki, T. Nebenvalenzringverbindungen. IV. Über einige innerkomplexe Kobaltsalze der Oxyaldimine. *Bull. Chem. Soc. Jpn.* **1938**, *13*, 252–260.

(6) Vogt, L. H.; Faigenbaum, H. M.; Wiberley, E. Synthetic Reversible Oxygen-Carrying Chelates. *Chem. Rev.* **1963**, *63*, 269–277.

(7) Basolo, F.; Hoffmann, M.; Ibers, A. Synthetic Oxygen Carriers of Biological Interest. *Acc. Chem. Res.* **1975**, *8*, 384–392.

(8) McLendon, G.; Martell, A. E. Inorganic Oxygen Carriers as Models for Biological Systems. *Coord. Chem. Rev.* **1976**, *19*, 1–39.

(9) Carter, M. J.; Rillema, D. P.; Basolo, F. Oxygen Carrier and Redox Properties of Some Neutral Cobalt Chelates. Axial and In-plane Ligand Effects. *J. Am. Chem. Soc.* **1974**, *96*, 392–400.

(10) Calvin, M. J. The Oxygen-Carrying Synthetic Chelate Compounds. *J. Am. Chem. Soc.* **1946**, *68*, 2254–2256.

(11) Ortiz, B.; Park, S.-M. Electrochemical and Spectroelectrochemical Studies of Cobalt Salen and Salophen as Oxygen Reduction Catalysts. *Bull. Korean Chem. Soc.* **2000**, *21*, 405–411.

(12) Floriani, C.; Calderazzo, F. Oxygen Adducts of Schiff's Base Complexes of Cobalt Prepared in Solution. *J. Chem. Soc. A* **1969**, 946–953.

(13) Ochiai, E.-I. Electronic Structure and Oxygenation of Bis-(salicylaldehyde)ethylenediimino cobalt(II). *J. Inorg. Nucl. Chem.* **1973**, *35*, 1727–1739.

(14) Ochiai, E.-I. Oxygenation of Cobalt(II) complexes. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3375–3389.

(15) McDowali, J. M.; Vincent, C. A. Viscosity Behaviour of Some Simple Electrolytes in Formamide Solution. *J. Chem. Soc., Faraday Trans.* **1974**, *1*, 1862–1868.

(16) Deck, M. R. J.; Bird, K. J.; Parker, A. Partial Molal Volumes of Single Ions in Protic and Dipolar Aprotic Solvents. *Aust. J. Chem.* **1975**, *28*, 955–963.

(17) Zhao, C.; Ma, P.; Li, J. Partial Molar Volumes and Viscosity *B*-coefficients of Arginine in Aqueous Glucose, Sucrose and L-ascorbic Acid Solutions at *T* = 298.15. *J. Chem. Thermodyn.* **2005**, *37*, 37–42.

(18) Timmermans, J. *Physico-Chemical Constants of Pure organic Compounds*; Elsevier: New York, 1950.

(19) Ismadji, S.; Djojoputro, H. Density and Viscosity of Binary Mixtures of Ethyl-2-methylbutyrate and Ethyl Hexanoate with Methanol, Ethanol, and 1-Propanol at (293.15, 303.15, and 313.15) K. *J. Chem. Eng. Data* **2005**, *50*, 1343–1347.

(20) Martin Contreras, S. Densities and Viscosities of Binary Mixtures of 1,4-dioxane with 1-propanol and 2-propanol at (25, 30, and 40) °C. *J. Chem. Eng. Data* **2001**, *46*, 1149–1152.

(21) Shoemaker, D. P.; Garland, C. W. S. *Experiments in Physical Chemistry*; McGraw Hill: New York, 1967.

(22) Roy, M. N.; Sinha, B.; Dey, R.; Sinha, A. Solute-Solvent and Solute-Solute Interactions of Resorcinol in Mixed 1,4-dioxane-water Systems at Different Temperatures. *Int. J. Thermophys.* **2005**, *26*, 1549–1563.

(23) Bailes, R. H.; Calvin, M. The Oxygen-Carrying Synthetic Chelate Compounds. VII. Preparation. *J. Am. Chem. Soc.* **1947**, *69*, 1886–1893.

(24) Kumar, D. N.; Garg, B. S. Some New Cobalt(II) Complexes Synthesis, Characterization and Thermal Studies. *J. Therm. Anal. Calorim.* **2002**, *69*, 607–616.

(25) Marsh, K. N. *Recommended reference materials for the realization of physicochemical properties*; Blackwell Scientific Publications: Oxford, U.K., 1987.

(26) Dean, J. A. *Lange's handbook of chemistry*, 11th ed.; McGraw-Hill Book Company: New York, 1973.

(27) Chatterjee, A.; Das, B. Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetraphenylborate, and Sodium Bromide in Methanol (1) + Water (2) Mixtures at (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data* **2006**, *51*, 1352–1355.

(28) Bhattacharjee, A.; Roy, M. N. Ion Association and Solvation Behavior of Tetraalkylammonium Iodides in Binary Mixtures of Dichloromethane + *N*,*N*-dimethylformamide Probed by a Conductometric Study. *Phys. Chem. Chem. Phys.* **2010**, *12*, 14534–14542.

(29) Roy, M. N.; Sinha, B.; Dakua, V. K. Excess Molar Volumes and Viscosity Deviations of Binary Liquid Mixtures of 1,3-Dioxolane and 1,4-Dioxane with Butyl Acetate, Butyric Acid, Butylamine, and 2-Butanone at 298.15 K. *J. Chem. Eng. Data* **2006**, *51*, 590–594.

(30) Roy, M. N.; Sinha, B. Viscous synergy and isentropic compressibility of some monoalkanols and cyclic ethers in water at 298.15 K. *J. Mol. Liq.* **2007**, *133*, 89–99.

(31) Covington, A. K.; Dickinson, T. *Physical chemistry of organic solvent systems*; Plenum: New York, 1973.

(32) Rodriguez-Cordoba, W; Zugazagoitia, J.; Collado-Fregoso, J. S.; Peon, E. J. Excited State Intramolecular Proton Transfer in Schiff Bases. Decay of the Locally Excited Enol State Observed by Femtosecond Resolved Fluorescence. *J. Phys. Chem. A* **2007**, *111*, 6241–6247.

(33) Harned, H. S.; Owen, B. B. *The physical chemistry of electrolytic solutions*, 3rd ed.; Reinhold Publishing Corporation: New York, 1964.

(34) Millero, F. J. *Water and Aqueous Solutions: Structure, Thermodynamics, and Transport Processes*; Horne, R. A., Ed.; Wiley-Interscience: New York, 1972.

(35) Parmar, M. L.; Banyal, D. S. Effect of temperatures on the partial molar volumes of some bivalent transition metal nitrates and magnesium nitrate in DMF + water mixtures. *Indian J. Chem.* **2005**, *44A*, 1582–1588.

(36) Hepler, L. G. Solute-solvent interactions of some salts in THF + water mixtures by volumetric measurements. *Can. J. Chem.* **1969**, *47*, 4617–4622.

(37) Jones, G.; Dole, D. The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride. *J. Am. Chem. Soc.* **1929**, *51*, 2950–2964.

(38) Feakins, D.; Freemantle, D. J.; Lawrence, K. G. Transition state treatment of the relative viscosity of electrolytic solutions. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 795–806.

(39) Glasston, S.; Laidler, K.; Eyring, H. *Theory of Rate Processes*; McGraw-Hill: New York, 1941.