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Solute–solvent and solvent–solvent interactions of menthol in isopropyl alcohol and its binary mixtures with methyl salicylate by volumetric, viscometric, interferometric and refractive index techniques

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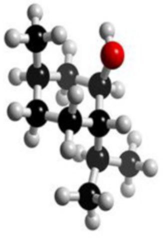
ABSTRACT

The apparent molar volume ($V_{\varnothing}$), viscosity *B*-coefficient, isentropic compressibility (ϕ_K) of menthol have been determined in binary solution of isopropyl alcohol and methyl salicylate (at 303.15, 313.15 and 323.15 K) from density (ρ), viscosity (η) and sound speed respectively. The apparent molar volumes have been extrapolated to zero concentration to obtain the limiting values at infinite dilution using Masson equation. The infinite dilution partial molar expansibilities have also been calculated from the temperature dependence of the limiting apparent molar volumes. Viscosity *B*-coefficients has been calculated using Jones–Dole equation. The structure-making or breaking capacity of the solute under investigation has been discussed in terms of sign of $(\delta^2 V_{\varnothing}^{o}/\delta T^2)_P$. The activation parameters of viscous flow were determined and discussed by application of transition state theory.

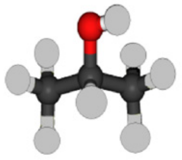
1. Introduction

The volumetric, viscometric and interferrometric behavior of solutes has been proved to be very useful in elucidating the various interactions occurring in pure and mixed solvents. Studies on the effect of concentration and temperature on the apparent molar volumes of solutes have been extensively used to obtain information on ion–ion, ion–solvent, and solvent–solvent interactions [1–3]. It has been found by a number of workers [4–6] that the addition of a solute could either make or break the structure of a liquid.

In this paper we have attempted to study the behavior of menthol in isopropyl alcohol (I.P.A.) and in its mixture with methyl salicylate (5, 10 and 15 mass%) at various temperatures because of their extensive use in pharmaceutical and cosmetic industries. Methyl salicylate has a long history of use in consumer products as a counterirritant and as an analgesic in the treatment and temporary management of aching and painful muscles and joints. Methyl salicylate is also used as an UV absorber and in perfumery as a modifier of blossom fragrances [7]. I.P.A. is widely used as a cleaning agent, a cost-effective preservative for biological specimens and is a major ingredient in "dry-gas" fuel additive. Menthol, an old remedy in Chinese medicine extracted from plants of the genus *Mentha*, is widely used as both a cooling agent and a counterirritant for relieving pain especially in the muscles, viscera or remote areas [8], as well as for the treatment of pruritus.



Menthol



Isopropyl alcohol

Methyl salicylate

2. Experimental

2.1. Chemicals

Menthol (Thomas Baker, >99%) was used as such without further purification. Isopropyl alcohol (Merck, >99.5%) and methyl salicylate (Sigma–Aldrich, >99%) were used with no further purification other than being dried with molecular sieves. Experimental values of viscosity (η), density (ρ), sound speed (u) and refractive indices (n_D) of the pure solvents were compared with the literature values and are listed in Table 1.

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Table 1
Density (ρ), viscosity (η), sound speed (u) and refractive indices (n_D) of binary mixture of methyl salicylate (1) and I.P.A. (2) at different temperatures.

Temperature (K)	$\rho \times 10^{-3}$ (kg m^{-3})		η (mPa s)		u (m s^{-1})		n_D	
	Exp	Lit	Exp	Lit	Exp	Lit	Exp	Lit
$w_1 = 0.00$								
303.15	0.7771	0.7768 [25]	1.7470	1.7430 [26]	1130.6	1127 [27]	1.3736	1.3737 [28]
313.15	0.7684	0.7680 [25]	1.3296	1.3260 [25]	–	–	–	–
323.15	0.7560	0.7557 [26]	1.0029	1.0020 [26]	–	–	–	–
$w_1 = 0.05$								
303.15	0.7909	–	1.7981	–	1146.8	–	1.3791	–
313.15	0.7828	–	1.3786	–	–	–	–	–
323.15	0.7703	–	1.0485	–	–	–	–	–
$w_1 = 0.10$								
303.15	0.8053	–	1.8464	–	1170.6	–	1.3852	–
313.15	0.7943	–	1.4369	–	–	–	–	–
323.15	0.7851	–	1.1164	–	–	–	–	–
$w_1 = 0.15$								
303.15	0.8224	–	1.9614	–	1197.7	–	1.3912	–
313.15	0.8120	–	1.5600	–	–	–	–	–
323.15	0.7993	–	1.2274	–	–	–	–	–

2.2. Measurements

Densities (ρ) were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of about 0.1 cm. The measurements were done in a thermostat bath controlled to ±0.01 K. Viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from literature. The flow times were accurate to ±0.1 s, and the uncertainty in the viscosity measurements was $\pm 2 \times 10^{-4}$ mPa s. The mixtures were prepared by mixing known volume of pure liquids in airtight-stopper bottles and each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of determining possible dispersion of the results obtained. Adequate precautions were taken to minimize evaporation loses during the actual measurements. Mass measurements were done on a Mettler AG-285 electronic balance with a precision of ±0.01 mg. The precision of density measurements was $\pm 3 \times 10^{-4}$ g cm^{-3}. Refractive index was measured with the help of Abbe-Refractometer (U.S.A.). The accuracy of refractive index measurement was ±0.0002 units. The refractometer was calibrated twice using distilled and deionized water, and calibration was checked after every few measurements.

Viscosity of the solution, η, is given by the following equation:

$$\eta = \left(\frac{Kt - L}{t}\right)\rho \qquad (1)$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within ±0.003 mPa s.

Details of the methods and techniques of density and viscosity measurements have been described elsewhere [9–12]. The solutions studied here were prepared by mass and the conversion of molality in molarity was accomplished [3] using experimental density values. The experimental values of concentrations (c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in Table 2.

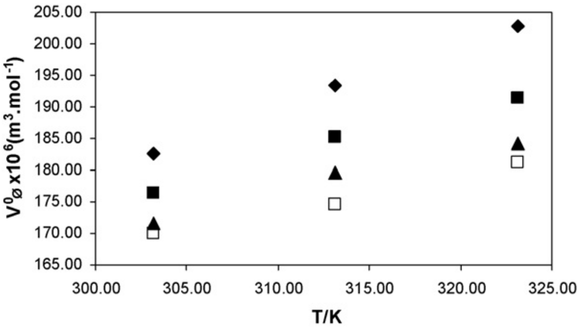


Fig. 1. Plot of $V^o_\emptyset \times 10^6$ (m^3 mol^{-1}) as a function of temperature (T, K) of menthol in 0% (♦), 5% (■), 10% (▲), 15% (□) mass percent of methyl salicylate + I.P.A.

3. Results and discussions

Apparent molar volumes ($V_\emptyset$) were determined from the solution densities using the following equation:

$$V^o_\emptyset = \frac{M}{\rho_o} - \frac{1000(\rho - \rho_o)}{c\rho_o} \qquad (2)$$

where M is the molar mass of the solute, c is the molarity of the solution; ρ_0 and ρ are the densities of the solvent and the solution respectively. The limiting apparent molar volumes $V^o_\emptyset$ was calculated using a least-square treatment to the plots of $V_\emptyset$ versus $\sqrt{c}$ using the Masson equation [13].

$$V_\emptyset = V^o_\emptyset + S^*_v\sqrt{c} \qquad (3)$$

where $V^o_\emptyset$ is the partial molar volume at infinite dilution and S^*_v the experimental slope. The plots of $V_\emptyset$ against square root of molar concentration ($\sqrt{c}$) were found to be linear with negative slopes. Values of $V^o_\emptyset$ and S^*_v are reported in Table 3.

The solute–solvent and solute–solute interactions can be interpreted in terms of structural changes which arise due to hydrogen bonding between various components of the solvent and solution systems. $V^o_\emptyset$ values can be used to interpret solute–solvent interactions. Table 3 reveals that $V^o_\emptyset$ values are positive and increases with rise in temperature and decreases with increase in the mass percent of methyl salicylate in the solvent mixture as depicted in Figs. 1 and 2 respectively. This indicates the presence of strong solute–solvent interactions and these interactions are strengthened with rise in temperature and weakened with an increase in the mass percent of methyl salicylate suggesting larger electrostriction at higher temperature. Similar results were obtained for some 1:1 electrolytes in aqueous DMF [14] and aqueous THF [15].

The observed result can also be explained in view of the molar volume of solute as well as solvents studied here. The partial molar volume (182.55) of menthol in pure I.P.A. is far greater than molar volume of I.P.A. (77.24) but a little extent greater than the molar

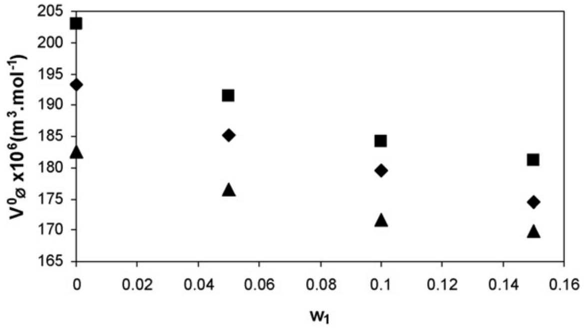
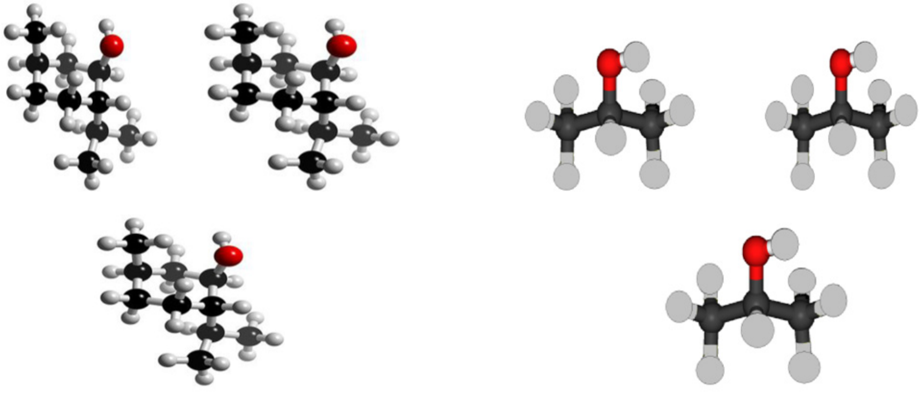


Fig. 2. Plot of $V^o_Ø \times 10^6$ (m^3 mol^{-1}) as a function of mass percent of methyl salicylate in different binary mixture of methyl salicylate + I.P.A. at 303.15 K (▲), 313.15 K (♦) and 323.15 K (■).

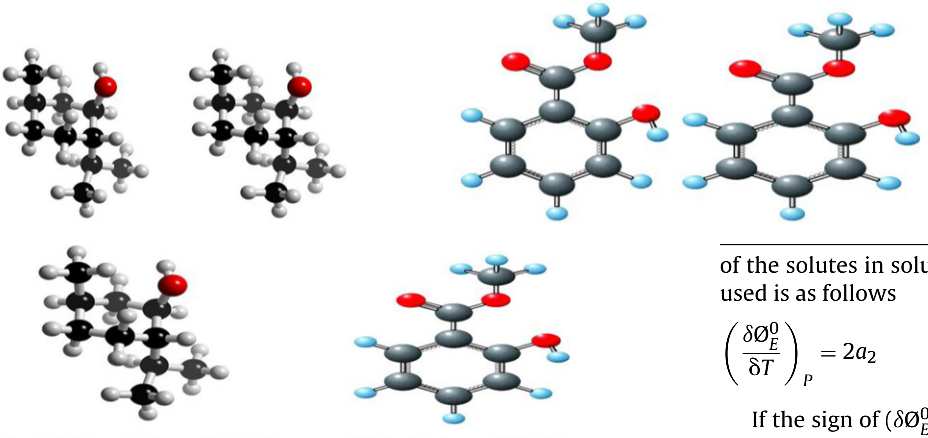
volume of methyl salicylate. Further, the partial molar volume of menthol decreases gradually with decreasing composition of I.P.A. to the mixture. Hence I.P.A. easily fits in menthol in the mixture resulting in more solute–solvent interaction between them which is an excellent agreement with the conclusion drawn from values of $V^o_Ø$ as well as viscosity *B*-coefficient.

A schematic diagram is shown below.



Partial Molar Volume (182.55)

Molar Volume (77.24)



Partial Molar Volume (182.55)

Molar Volume (129.49)

S^*_v values are negative at all temperatures and the values decreases with increase of temperature and increases with increase in mass percent of methyl salicylate which may be attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of ion–ion interactions (ionic-dissociation) [16]. The magnitude of $V^o_Ø$ values are much greater than those of S^*_v for all the solutions which suggests that solute–solvent interactions dominate over solute–solute interactions in all the solutions and at all experimental temperatures.

The polynomial below represents the variation of $V^o_Ø$ with temperature

$$V^o_Ø = a_0 + a_1 T + a_2 T^2 \tag{4}$$

over the temperature range under study where *T* is the temperature in K. Values of coefficients of the above equation are reported in Table 4.

The apparent molar expansibilities ($Ø^0_E$) can be obtained by the following equation:

$$Ø^0_E = \left(\frac{\delta V^o_Ø}{\delta T}\right)_P = a_1 + 2a_2 T \tag{5}$$

The values $Ø^0_E$ of for different solutions at 303.15, 313.15 and 323.15 K are reported in Table 5. Table 5 reveals that $Ø^0_E$ value decreases with increasing temperature and mass percent of methyl salicylate. This fact may be attributed to gradual disappearance of caging or packing effect [16,17] in the ternary solutions. According to Helper [18] the sign of $(\delta Ø^0_E/\delta T)_P$ is a better criterion in characterizing the long-range structure-making and breaking ability of the solutes in solution. The general thermodynamic expression used is as follows

$$\left(\frac{\delta Ø^0_E}{\delta T}\right)_P = 2a_2 \tag{6}$$

If the sign of $(\delta Ø^0_E/\delta T)_P$ is positive [19] the solute is a structure maker and if negative it is a structure breaker. As is evident from the values of $(\delta Ø^0_E/\delta T)_P$, menthol predominately acts as a structure breaker.

The viscosity data has been analyzed using Jones–Dole [20] equation:

$$\left(\frac{(\eta/\eta_0 - 1)}{c^{1/2}}\right) = A + Bc^{1/2} \tag{7}$$

Table 2
Molarity (c), density (ρ), viscosity (η), apparent molar volume ($V_{\varnothing}$) and $(\eta/\eta_0 - 1)/c^{1/2}$ of menthol in binary mixture of different mass% (w_1) of methyl salicylate (1) and I.P.A. (2) at 303.15, 313.15 and 323.15 K.

c (mol dm^{-3})	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	$V_{\varnothing} \times 10^6$ (m^3 mol^{-1})	$(\eta/\eta_0 - 1)/c^{1/2}$
$w_1 = 0.00$				
303.15 K				
0.0250	0.7776	1.7572	176.31	0.0370
0.0350	0.7778	1.7613	175.36	0.0436
0.0450	0.7780	1.7659	174.55	0.0510
0.0550	0.7783	1.7713	173.92	0.0593
0.0750	0.7788	1.7812	172.25	0.0716
0.0850	0.7791	1.7851	171.03	0.0748
313.15 K				
0.0247	0.7688	1.3401	182.60	0.0501
0.0346	0.7690	1.3443	180.77	0.0592
0.0445	0.7692	1.3493	178.95	0.0699
0.0544	0.7695	1.3545	177.14	0.0800
0.0742	0.7700	1.3638	175.43	0.0942
0.0840	0.7703	1.3684	173.20	0.1007
323.15 K				
0.0243	0.7564	1.0121	187.30	0.0590
0.0340	0.7566	1.0170	184.80	0.0760
0.0438	0.7568	1.0215	181.50	0.0886
0.0535	0.7571	1.0258	179.20	0.0989
0.0730	0.7577	1.0342	175.65	0.1157
0.0827	0.7580	1.0388	174.40	0.1246
$w_1 = 0.05$				
303.15 K				
0.0250	0.7914	1.8073	171.15	0.0322
0.0350	0.7917	1.8110	170.20	0.0384
0.0450	0.7919	1.8145	169.06	0.0431
0.0550	0.7922	1.8200	168.34	0.0519
0.0750	0.7927	1.8282	167.30	0.0612
0.0850	0.7930	1.8329	166.55	0.0664
313.15 K				
0.0247	0.7832	1.3879	176.43	0.0430
0.0346	0.7835	1.3922	174.00	0.0530
0.0445	0.7837	1.3966	172.70	0.0620
0.0544	0.7840	1.4014	171.45	0.0709
0.0741	0.7846	1.4097	169.32	0.0829
0.0840	0.7849	1.4138	168.40	0.0881
323.15 K				
0.0243	0.7707	1.0567	182.04	0.0500
0.0340	0.7709	1.0603	180.44	0.0610
0.0438	0.7711	1.0642	178.83	0.0715
0.0535	0.7714	1.0682	177.33	0.0811
0.0729	0.7719	1.0754	175.24	0.0950
0.0827	0.7721	1.0795	174.24	0.1030
$w_1 = 0.10$				
303.15 K				
0.0250	0.8058	1.8631	168.90	0.0571
0.0350	0.8060	1.8675	168.40	0.0610
0.0450	0.8062	1.8728	167.96	0.0673
0.0550	0.8065	1.8794	167.76	0.0760
0.0750	0.8069	1.8878	166.94	0.0818
0.0850	0.8072	1.8937	166.57	0.0879
313.15 K				
0.0247	0.7948	1.4511	172.80	0.0630
0.0345	0.7950	1.4572	171.06	0.0760
0.0444	0.7952	1.4605	170.24	0.0780
0.0543	0.7955	1.4673	168.94	0.0910
0.0740	0.7960	1.4767	167.40	0.1020
0.0839	0.7963	1.4821	166.88	0.1086
323.15 K				
0.0244	0.7855	1.1281	175.71	0.0670
0.0341	0.7858	1.1328	173.71	0.0800
0.0439	0.7860	1.1362	172.20	0.0850
0.0536	0.7862	1.1414	171.80	0.0970
0.0731	0.7868	1.1501	169.65	0.1120
0.0829	0.7871	1.1535	167.87	0.1160
$w_1 = 0.15$				
303.15 K				
0.0250	0.8228	1.9763	168.21	0.0480
0.0350	0.8230	1.9818	167.94	0.0554
0.0450	0.8232	1.9859	167.71	0.0588
0.0550	0.8235	1.9905	167.44	0.0632
0.0750	0.8238	1.9991	166.98	0.0702
0.0850	0.8240	2.0034	166.83	0.0734
313.15 K				
0.0247	0.8125	1.5752	169.49	0.0620
0.0346	0.8127	1.5806	168.51	0.0710
0.0444	0.8129	1.5846	167.48	0.0750
0.0543	0.8132	1.5909	166.69	0.0850
0.0741	0.8137	1.6003	165.80	0.0949
0.0840	0.8140	1.6047	165.00	0.0990
323.15 K				
0.0243	0.7997	1.2408	175.44	0.0700
0.0340	0.7999	1.2451	174.28	0.0781
0.0437	0.8001	1.2500	173.37	0.0880
0.0535	0.8003	1.2538	172.68	0.0931
0.0729	0.8007	1.2634	171.20	0.1087
0.0826	0.8010	1.2683	170.48	0.1160

where η_0 and η are the viscosities of the solvent/solvent mixtures and solution respectively. A and B are the constants estimated by a least-squares method and are reported in Table 6. The values of the A coefficient are found to decrease with temperature and increases with increase in mass percent of methyl salicylate. These results indicate the presence of very weak ion–ion interactions and these interactions further decrease with the rise of experimental temperatures and increase with an increase in mass percent of methyl salicylate. These results are in excellent agreement with those obtained from S_v^* values.

The effects of ion–solvent interactions on the solution viscosity can be inferred from the B-coefficient [21,22]. The viscosity B-coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 6 it is evident that the values of the B-coefficient are positive, thereby suggesting the presence of strong solute–solvent interactions, and these types of interactions are strengthened with a rise in temperature and weakened with an increase of mass percent of methyl salicylate. Similar results are obtained from $V_{\emptyset}^{o}$ values discussed earlier.

The adiabatic compressibility (β) was evaluated from the following equation:

$$\beta = \frac{1}{u^2 \rho} \tag{8}$$

where ρ is the solution density and u is the sound speed in the solution. The apparent molal adiabatic compressibility ($\varnothing_K$) of the solutions was determined from the relation,

$$\emptyset_K = \frac{M\beta}{\rho_o} + \frac{1000(\beta\rho_o - \beta_o\rho)}{m\rho\rho_o} \tag{9}$$

where β_o, β are the adiabatic compressibility of the solvent and solution respectively and m is the molality of the solution. Limiting partial molal adiabatic compressibilities ($\emptyset_K^o$) and experimental slopes (S_K^*) were obtained by fitting $\varnothing_K$ against the square root of molality of the electrolyte ($\sqrt{m}$) using the method of least squares.

$$\emptyset_K = \emptyset_K^o + S_K^* \sqrt{m} \tag{10}$$

Values of m, u, β, $\varnothing_K$, $\emptyset_K^o$ and S_K^* are presented in Table 7. Since the values of $\emptyset_K^o$ and S_K^* are measures of ion–solvent and ion–ion

Table 3
Limiting apparent molar volumes ($V_{\varnothing}^{o}$) and experimental slopes (S_v^*) of menthol in binary mixture of different mass% (w_1) of methyl salicylate (1) and I.P.A. (2) at 303.15, 313.15 and 323.15 K.

Mass% of methyl salicylate	$V_{\varnothing}^{o} \times 10^6$ (m^3 mol^{-1})			$S_v^* \times 10^6$ (m^3 mol$^{-3/2}$ dm$^{3/2}$)		
	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
$w_1 = 0.00$	182.55	193.33	202.89	–38.25	–68.07	–100.44
$w_1 = 0.05$	176.45	185.26	191.37	–33.97	–58.74	–59.83
$w_1 = 0.10$	171.63	179.53	184.13	–17.15	–44.36	–55.16
$w_1 = 0.15$	169.92	174.58	181.18	–10.60	–33.01	–37.10

Table 4
Values of the coefficients of Eq. (4) of menthol in binary mixture of different mass% (w_1) of methyl salicylate (1) and I.P.A. (2) at 303.15, 313.15 and 323.15 K.

Mass % of methyl salicylate	a_0 (m^3 mol^{-1})	a_1 (m^3 mol^{-1})	a_2 (m^3 mol^{-1} K^{-2})
$w_1 = 0.00$	–723.33	4.84	–0.0061
$w_1 = 0.05$	–1381.70	9.26	–0.0136
$w_1 = 0.10$	–1624.40	10.90	–0.0164
$w_1 = 0.15$	–1734.70	11.65	–0.0177

Table 5
Limiting partial molar expansibilities of menthol in binary mixture of different mass% (w_1) of methyl salicylate (1) and I.P.A. (2) at 303.15, 313.15 and 323.15 K.

Mass % of methyl salicylate	$\varnothing_E^0$ (m^3 mol^{-1} K^{-1})			$(\delta\varnothing_E^0/\delta T)_P$ dm^3 mol^{-1} K^{-2}
	303.15 K	313.15 K	323.15 K	
$w_1 = 0.00$	1.1390	1.0170	0.8950	–0.0122
$w_1 = 0.05$	1.0170	0.7450	0.4730	–0.0272
$w_1 = 0.10$	0.9527	0.6247	0.2967	–0.0328
$w_1 = 0.15$	0.9175	0.5635	0.2095	–0.0354

interactions respectively, a perusal of Table 7 shows that the values are in agreement with those drawn from the values of $V_{\varnothing}^{o}$ and S_v^* discussed earlier.

The viscosity data has also been analyzed on the basis of transition state theory of relative viscosity of solutes as suggested by Feakins et al. [23] using the following equation

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + \frac{(1000B + \bar{V}_2^0 - \bar{V}_1^0)\,RT}{\bar{V}_1^0} \tag{11}$$

Table 6
Values of A and B coefficients of menthol in binary mixture of different mass% (w_1) of methyl salicylate (1) and I.P.A.(2) at 303.15, 313.15 and 323.15 K.

Mass % of methyl salicylate	A (dm$^{3/2}$ mol$^{-1/2}$)			B (dm^3 mol^{-1})		
	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
$w_1 = 0.00$	–0.0108	–0.0118	–0.0149	0.2965	0.3888	0.4871
$w_1 = 0.05$	–0.0101	–0.0105	–0.0126	0.2606	0.3428	0.4015
$w_1 = 0.10$	0.0187	0.0106	0.0086	0.2349	0.3376	0.3795
$w_1 = 0.15$	0.0196	0.0177	0.0144	0.1821	0.2823	0.3495

Table 7
Molality (m), sound speed (u), adiabatic compressibility (β), partial molal adiabatic compressibility ($\varnothing_K$), limiting partial adiabatic compressibility ($\varnothing_K^o$), experimental slope (S_K^*) and refractive indices of menthol in binary mixture of different mass% (w_1) of methyl salicylate (1) and I.P.A.(2) at 303.15 K.

m (mol kg^{-1})	u (m s^{-1})	$\beta \times 10^{10}$ (Pa^{-1})	$\varnothing_K \times 10^{10}$ (m^3 mol^{-1} Pa^{-1})	$\varnothing_K^o \times 10^{10}$ (m^3 mol^{-1} Pa^{-1})	$S_K^* \times 10^{10}$ (m^3 mol$^{-3/2}$ Pa^{-1} kg$^{1/2}$)	n_D
$w_1 = 0.00$						
0.0323	1135.7	9.9707	–2.0794	–0.5097	–8.7395	1.3741
0.0453	1138.2	9.9242	–2.3166			1.3744
0.0584	1141.2	9.8692	–2.6390			1.3747
0.0715	1144.4	9.8106	–2.9100			1.3750
0.0978	1151.1	9.6908	–3.2796			1.3755
0.1110	1154.2	9.6350	–3.3568			1.3757
$w_1 = 0.05$						
0.0317	1152.0	9.5213	–2.0600	–0.7934	–7.2134	1.3796
0.0445	1154.7	9.4744	–2.3500			1.3799
0.0573	1157.3	9.4282	–2.5000			1.3801
0.0702	1160.4	9.3756	–2.7132			1.3803
0.0960	1166.8	9.2658	–3.0300			1.3807
0.1090	1170.3	9.2080	–3.1700			1.3809
$w_1 = 0.10$						
0.0312	1176.4	8.9674	–2.0200	–0.8666	–6.2585	1.3852
0.0437	1178.8	8.9278	–2.1500			1.3858
0.0563	1181.7	8.8825	–2.3300			1.3861
0.0689	1184.6	8.8368	–2.4700			1.3865
0.0943	1191.2	8.7328	–2.8000			1.3870
0.1071	1194.9	8.6776	–2.9416			1.3872
$w_1 = 0.15$						
0.0305	1203.4	8.3926	–1.6900	–0.9136	–4.1905	1.3920
0.0428	1205.6	8.3602	–1.7300			1.3924
0.0551	1208.2	8.3219	–1.8900			1.3928
0.0675	1210.8	8.2833	–2.0000			1.3932
0.0924	1216.7	8.2000	–2.1935			1.3937
0.1048	1219.7	8.1572	–2.2800			1.3940

Table 8
Values of $\Delta\mu_1^{0\#}$, $\Delta\mu_2^{0\#}$, $T\Delta S_2^{0\#}$ and $\Delta H_2^{0\#}$ of menthol in binary mixture of different mass% (w_1) of methyl salicylate (1) and I.P.A. (2) at 303.15, 313.15 and 323.15 K.

Parameter	303.15 K	313.15 K	323.15 K
$w_1 = 0.00$			
$\Delta\mu_1^{0\#}$, kJ mol^{-1}	66.92	68.45	69.92
$\Delta\mu_2^{0\#}$, kJ mol^{-1}	13.16	16.84	20.70
$T\Delta S_2^{0\#}$, kJ mol^{-1}	−114.35	−118.12	−121.89
$\Delta H_2^{0\#} \times 10^3$ kJ mol^{-1}	−101.19	−101.28	−101.19
$w_1 = 0.05$			
$\Delta\mu_1^{0\#}$, kJ mol^{-1}	67.03	68.58	70.07
$\Delta\mu_2^{0\#}$, kJ mol^{-1}	11.60	14.83	17.18
$T\Delta S_2^{0\#}$, kJ mol^{-1}	−84.55	−87.34	−90.13
$\Delta H_2^{0\#} \times 10^3$ kJ mol^{-1}	−72.94	−72.51	−72.95
$w_1 = 0.10$			
$\Delta\mu_1^{0\#}$, kJ mol^{-1}	67.13	68.73	70.31
$\Delta\mu_2^{0\#}$, kJ mol^{-1}	10.45	14.18	15.17
$T\Delta S_2^{0\#}$, kJ mol^{-1}	−89.70	−92.66	−76.26
$\Delta H_2^{0\#} \times 10^3$ kJ mol^{-1}	−79.26	−78.48	−61.10
$w_1 = 0.15$			
$\Delta\mu_1^{0\#}$, kJ mol^{-1}	67.31	68.97	70.58
$\Delta\mu_2^{0\#}$, kJ mol^{-1}	8.68	12.08	14.63
$T\Delta S_2^{0\#}$, kJ mol^{-1}	−90.13	−93.10	−96.07
$\Delta H_2^{0\#} \times 10^3$ kJ mol^{-1}	−81.45	−81.02	−81.45

where $\bar{V}_1^0$ and $\bar{V}_2^0$ are the partial molar volumes of the solvent and the solute respectively. The contribution per mole of the solute to the free energy of activation of viscous flow ($\Delta\mu_2^{0\#}$) of the solutions was determined from the above relation and is listed in Table 8. The free energy of activation of viscous flow of the pure solvent ($\Delta\mu_1^{0\#}$) is given by the relation:

$$\Delta\mu_1^0 = \Delta G_1^0 = \frac{RT\ln(\eta_0\bar{V}_1^0)}{hN_0} \tag{12}$$

where the symbols have their usual significance. The values of $\Delta\mu_2^{0\#}$ and $\Delta\mu_1^{0\#}$ are reported in Table 8. From Table 8 it is evident that $\Delta\mu_1^{0\#}$ is almost constant over all solvent composition and temperature, implying that $\Delta\mu_2^{0\#}$ is mainly dependent on the viscosity *B*-coefficients and $(\bar{V}_2^0 - \bar{V}_1^0)$ terms. According to Feakins et al., $\Delta\mu_2^{0\#} > \Delta\mu_1^{0\#}$ for electrolytes having positive *B*-coefficients and indicates a stronger solute–solvent interactions, thereby suggesting that the formation of transition state is accompanied by the rupture and distortion of the intermolecular forces in solvent structure [24]. The smaller values of $\Delta\mu_2^{0\#}$ supports the increased structure breaking tendency of the solute as discussed earlier. The entropy of activation for solution has been calculated using the following relation [23].

$$\Delta S_2^{0\#} = \frac{-\mathrm{d}(\Delta\mu_2^{0\#})}{\mathrm{d}T} \tag{13}$$

where $\Delta S_2^{0\#}$ has been determined from the negative slope of the plots of $\Delta\mu_2^{0\#}$ against *T* by using a least square treatment.

The activation enthalpy ($\Delta H_2^{0\#}$) has been calculated using the relation [23]:

$$\Delta H_2^{0\#-} = \Delta\mu_2^{0\#} + T\Delta S_2^{0\#} \tag{14}$$

The value of $\Delta S_2^{0\#}$ and $\Delta H_2^{0\#}$ are listed in Table 8 and are found to be negative for all the solutions at all experimental temperatures which suggest that the transition state is associated with bond-breaking and increase in order which supports our earlier discussions.

4. Conclusion

The values of apparent molar volume ($V_{\O}^{o}$), viscosity *B*-coefficients and isoentropic compressibility ($\O_{K}^{o}$) indicate the presence of strong solute–solvent interactions and these interactions are strengthened at higher temperature and weakened with increasing mass percent of methyl salicylate in the binary solution.

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