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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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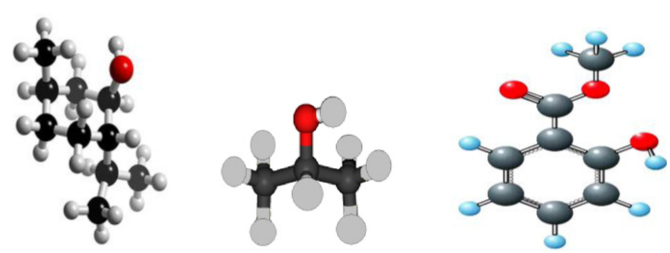
ABSTRACT

The apparent molar volume ($V_\varnothing$), viscosity *B*-coefficient, isoentropic 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 $(\delta^2 V^o_\varnothing/\delta T^2)_p$. 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 $\pm$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 $\pm$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 $\pm$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 $\pm$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:

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

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

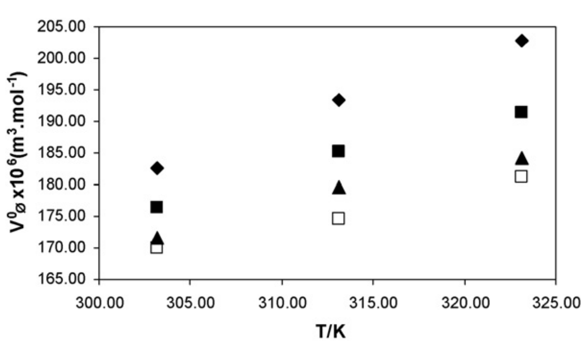

Fig. 1. Plot of $V^o_\varnothing \times 10^6$ (m^3 mol^{-1}) as a function of temperature (T, K) of menthol in 0% (♦), 5% (■), 10% (▲), 15% (□) mass percent of methyl salicylate + I.P.A.

liquid, respectively. The uncertainty in viscosity measurements is within $\pm$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.

3. Results and discussions

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

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

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 $V^o_\varnothing$ was calculated using a least-square treatment to the plots of $V_\varnothing$ versus $\sqrt{c}$ using the Masson equation [13].

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

where $V^o_\varnothing$ is the partial molar volume at infinite dilution and S^*_v the experimental slope. The plots of $V_\varnothing$ against square root of molar concentration ($\sqrt{c}$) were found to be linear with negative slopes. Values of $V^o_\varnothing$ 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. $V^o_\varnothing$ values can be used to interpret solute–solvent interactions. Table 3 reveals that $V^o_\varnothing$ 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