

Densities and Viscosities of Thymol + 1,8-Cineole

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Densities and viscosities of 1,8-cineole and of binary mixtures of thymol (1) + 1,8-cineole (2) were measured in the concentration range $x_1 = 0.58-0.71$ for temperatures between 278.15 and 298.15 K. Excess molar volumes derived from the experimental density data are negative at all temperatures and compositions and were fitted to a Redlich-Kister-type equation. The McAllister method was used to correlate the kinematic viscosities.

Introduction

Thymol is a terpenic alcohol with several pharmaceutical uses which can be obtained from rectified thyme oil (*Thymus vulgaris* L. var. *capitatus*). The two main components of the distilled oil, thymol (58-70 mass %) and 1,8-cineole, exhibit a double eutectic solid-liquid phase diagram (1), thus making crystallization a potentially interesting technique for the production of high-grade thymol.

In order to predict the behavior of the system in the crystallizer, especially in what concerns slurry transportation, some physical mathematical models may be used (2), thus requiring some data on the physical and transport properties of the system.

Therefore, in this study the densities and viscosities of binary mixtures of thymol (1) + 1,8-cineole (2) were measured in the range $x_1 = 0.58-0.71$ for temperatures between 278.15 and 298.15 K. Density and viscosity data for pure 1,8-cineole were also obtained in the same temperature range. From the experimental densities excess molar volumes were derived at all temperatures and compositions.

Experimental Section

Materials. Analytical grade thymol (Merck, >99 mass %) and 1,8-cineole (Fluka, 99 mol %) were used without any additional purification. Solutions were prepared by mass accurate to ± 0.1 mg using screw-capped Pyrex tubes. The compositions are accurate to ± 0.0001 in mole fraction.

Density Measurements. The experimental obtention of the density of saturated or metastable melts using a vibrating-tube densimeter is often difficult or impossible due to rapid and uncontrolled freezing of the sample (thus resulting in the damage of the equipment). For these types of systems the standard pycnometer technique, although less accurate, can have some advantages, since densities can be measured well into the metastable zone.

In this study, the densities of pure 1,8-cineole and of some binary mixtures were measured near saturation temperatures with a pycnometer and a Paar vibrating tube densimeter. In order to evaluate the reliability of the measurements, both sets of data were also compared.

Pycnometry experiments were performed with a 25 cm³ pycnometer calibrated at each temperature with distilled water. Prior to any reading, the solution contained in the pycnometer was allowed a period of 40 min for temperature equilibration. The thermostated bath, Haake KT52, equipped with an auxiliary cooler, Haake T53, was filled with ethanol and controlled to within ± 0.01 K. Temperatures were measured with a mercury-in-glass thermometer, E 0.1/0/50

Table 1. Density (ρ) and Absolute Viscosity (η) Data for 1,8-Cineole at Various Temperatures

T/K	ρ /(g·cm ⁻³)		η /(mPa·s)
	densimetry	pycnometry	
278.15	0.937 48	0.937 60	4.138
283.15	0.933 10	0.933 25	3.595
288.15	0.928 78	0.928 54	3.127
293.15	0.924 51	0.924 70	2.697
298.15	0.920 29	0.920 09	2.303

Table 2. Parameters of Eqs 1 and 2 and the Standard Deviation (σ)

	parameter	σ
equation 1	$T_0 = 278.15$ K $\rho_0 = 0.937 426$ g·cm ⁻³ $\beta = -8.594 \times 10^{-4}$ g·cm ⁻³ ·K ⁻¹	0.000 057 g·cm ⁻³
equation 2	$b_1 = -242.1934$ $b_2 = -7.99 \times 10^8$ $b_3 = 0.2914$ $b_4 = 55 552.67$	0.022 mPa·s

Table 3. Density (ρ) Data for Thymol (1) + 1,8-Cineole (2) at Various Temperatures

x_1	ρ /(g·cm ⁻³)				
	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K
Values Measured by Densimetry					
0.5865	0.976 26	0.972 28	0.968 21	0.964 25	0.960 25
0.6068	0.976 88	0.972 89	0.968 77	0.964 87	0.960 99
0.6272	0.977 87	0.973 88	0.969 82	0.965 89	0.961 89
0.6462	0.978 60	0.974 52	0.970 54	0.966 62	0.962 68
0.6661	0.979 06	0.974 99	0.971 01	0.967 09	0.963 11
0.6858			0.971 73	0.967 81	0.963 96
0.7057			0.972 31	0.968 40	0.964 42
Values Measured by Pycnometry					
0.5865	0.974 98				
0.6068	0.975 97				
0.6272	0.977 06				
0.6413	0.977 53				
0.6462	0.977 86	0.974 28	0.969 91	0.966 38	
0.6481					0.963 31
0.6560		0.974 52			
0.6661		0.974 59	0.970 38	0.967 07	0.963 93
0.6867			0.970 76	0.967 54	0.964 43
0.7057			0.971 25	0.968 10	0.965 05

DIN 12775, with a resolution of ± 0.05 K. This thermometer was calibrated against the melting and normal boiling points of distilled water (maximum accuracy of ± 0.05 K).

The densities were also measured using the mechanical oscillator densimeter, Chempro/Par DMA 60, equipped with an external measuring cell, Chempro/Par DMA 602. The density cell was water jacketed and the temperature kept constant to ± 0.05 K by means of a water bath, Haake C, equipped with a controller, Haake F3. The temperature was

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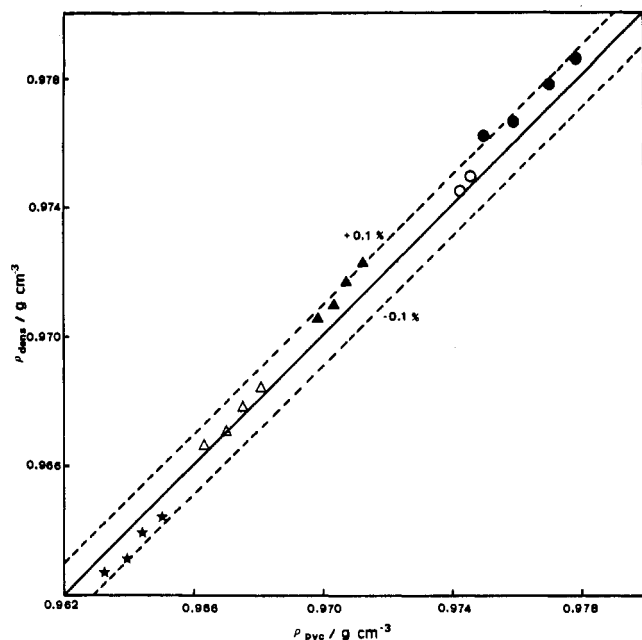


Figure 1. Density experimental data obtained by densimetry vs pycnometry values: (●) 278.15 K, (○) 283.15 K, (▲) 288.15 K, (△) 293.15 K, (★) 298.15 K.

Table 4. Absolute Viscosity (η) Data for Thymol (1) + 1,8-Cineole (2) at Various Temperatures

x_1	η /(mPa·s)				
	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K
0.5865	194.89	111.98	68.17	43.71	29.92
0.6068	206.97	115.35	71.01	45.56	30.80
0.6272	214.92	119.66	72.10	46.15	31.35
0.6462	219.88	122.95	73.17	46.86	31.41
0.6661	219.35		72.67	46.28	31.27
0.6858			71.95	45.95	30.92
0.7057			68.70	44.22	29.82

measured with a Pt resistance thermometer coupled to a 6800 Comark microprocessor with a ± 0.05 K resolution. The Pt resistance thermometer was calibrated to the IPTS-68 scale over the temperature range 263–323 K and estimated to be accurate to ± 0.08 K. The density was determined by the two-parameter equation $\rho = A + B\tau^2$, where ρ is the liquid density and τ is the period of oscillation. The best values of the parameters A and B were determined at each temperature by using various chemicals with well-established densities: deionized water (3), ethyl acetate (Fluka, >99 mass %) (4), *p*-xylene (Merck, >99.76 mass %) (5), ethanol (Merck, >99.8 mass %) (6), and benzene (Carlo Erba, >99.55 mass %) (7).

All density data reported in this study represent the average value of triplicate measurements with an accuracy of ± 0.00005 g·cm⁻³ for pycnometry and of ± 0.00001 g·cm⁻³ for densimetry.

Viscosity Measurements. Kinematic viscosities were obtained at the same temperatures and for the same mixtures used for density measurements from flow times by using standard Ubbelohde viscometers: Technico VHB-590, size 1 (0.01×10^{-6} m²·s⁻¹; range $(2-10) \times 10^{-6}$ m²·s⁻¹), for 1,8-cineole and Technico VHB-590, size 2C (0.3×10^{-6} m²·s⁻¹; range $(60-300) \times 10^{-6}$ m²·s⁻¹), for the binary mixtures. The experimental procedure was the same as for the pycnometry experiments. To check the manufacturer's calibration constants, the viscometers were recalibrated taking into account the kinetic-end effects: against deionized water (3) and benzene (7) for the viscometer of 0.01×10^{-6} m²·s⁻¹; against ethylene glycol (Merck, >99.5 mass %) (8, 9) and an 80 mass % glycerol + water (3, 10) for the viscometer of 0.3×10^{-6} m²·s⁻¹. The viscosity measurements represent the average values of at

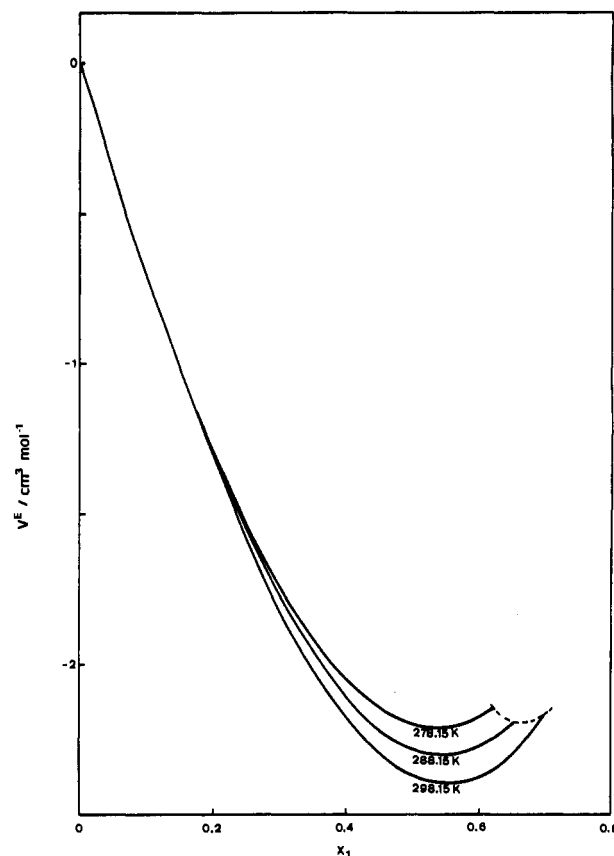


Figure 2. Calculated variation of the excess molar volume for thymol (1) + 1,8-cineole (2) at 278.15, 288.15, and 298.15 K. The dotted line concerns the liquid metastable zone.

Table 5. Parameters of Eq 1 for Thymol (ρ_1) and Fitting Constants for A_0 and A_1 in Eq 6

	ρ_0 /(g·cm ⁻³)	β /(g·cm ⁻³ ·K ⁻¹)	T_0 /K
ρ_1	0.981 787	-8.21×10^{-4}	278.15
	$\alpha_{1,j}$	$\alpha_{2,j}$	$\alpha_{3,j}$
A_0	0.999 136	0.879 64	-0.034 78
A_1	1.889 596	-9.371 95	0.038 50

least four readings per sample and are estimated to be accurate to within $\pm 0.50 \times 10^{-6}$ m²·s⁻¹. The absolute viscosity was computed from the measured kinematic viscosity and density, with an accuracy of ± 0.48 mPa·s.

The viscosities of samples containing very high contents of thymol could not be obtained for the lower temperatures investigated because those mixtures fall well into the solid-liquid metastable zone of the system (1).

Results and Discussion

1,8-Cineole. Experimental results of densities and viscosities at various temperatures are shown in Table 1.

The densities of 1,8-cineole measured by pycnometry are in quite good agreement with the densimeter data, showing a random distribution around these values and a maximum deviation of 0.000 24 g·cm⁻³.

The density of 1,8-cineole was described by the empirical equation

$$\rho/(\text{g}\cdot\text{cm}^{-3}) = \rho_0 + \beta((T/\text{K}) - T_0) \quad (1)$$

where ρ_0 is the density at the reference temperature T_0 and β a constant related to the thermal expansion. The parameters ρ_0 and β , Table 2, were obtained through the regression of the experimental values.

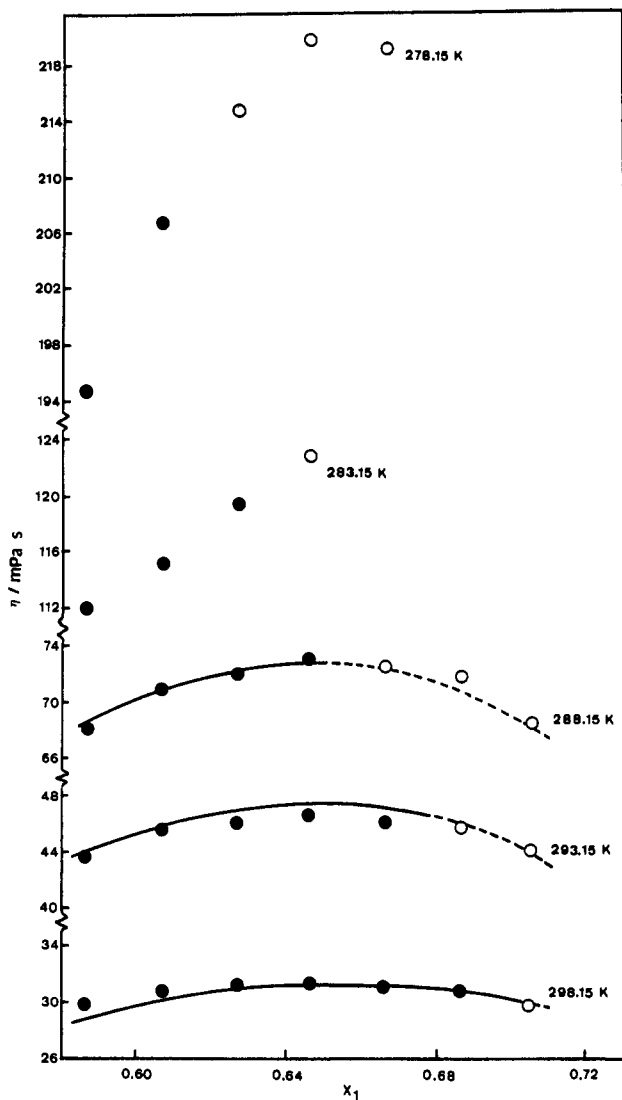


Figure 3. Absolute viscosity for thymol (1) + 1,8-cineole (2) at various temperatures: (●) experimental values; (—) calculated by the McAllister method. Open symbols (○) and dotted lines concern the liquid metastable zone.

Table 6. Andrade Parameters A_{ij} and B_{ij} for the Pseudoviscosities ν_1 , ν_{12} , and ν_{21}

	ν_1	ν_{12}	ν_{21}
A_{ij}	-20.5683	-13.6506	-36.519
B_{ij}	6346.805	6097.55	11177.44

To describe the temperature dependency of the absolute viscosity, we considered several empirical equations (10, 11). The best fit was obtained with the Chen–Pearlstein equation

$$\ln(\eta / (\text{mPa}\cdot\text{s})) = b_1 + b_2/(T/\text{K})^3 + b_3(T/\text{K}) + b_4/(T/\text{K}) \quad (2)$$

The values obtained for the parameters b_j are also listed in Table 2.

Binary Mixtures. The experimental values of densities and absolute viscosities for thymol (1) + 1,8-cineole (2), at different temperatures, are given in Tables 3 and 4.

Figure 1 is a parity plot of the experimental densimetry values vs those obtained by pycnometry. For 90% of these data the relative average deviations are always less than 0.1%, but except at 298.15 K, the pycnometry values are systematically lower than the densities measured with the Paar densimeter.

Excess molar volumes of liquid mixtures can be calculated from density measurements and composition using the equation

$$V_m^E = \frac{x_1 M_1 + (1-x_1)M_2}{\rho_m} - \frac{x_1 M_1}{\rho_1} - \frac{(1-x_1)M_2}{\rho_2} \quad (3)$$

where x_1 is the mole fraction of thymol, M_i and ρ_i are the molecular mass and the density of the pure liquid i , and ρ_m is the density of the binary mixture. However, since thymol is a solid in the range of temperatures studied, eq 3 cannot be directly used to obtain the excess molar volumes. Therefore, the dependence of V_m^E on the mole fraction was fitted to the Redlich–Kister equation

$$V_m^E/(\text{cm}^3 \text{mol}^{-1}) = x_1(1-x_1) \sum_{j=0}^n A_j(1-2x_1)^j \quad (4)$$

thus allowing the density of the binary mixtures to be described as

$$\rho_m = \frac{x_1 M_1 + (1-x_1)M_2}{\frac{x_1 M_1}{\rho_1} + \frac{(1-x_1)M_2}{\rho_2} + x_1(1-x_1) \sum_{j=0}^n A_j(1-2x_1)^j} \quad (5)$$

The empirical parameters A_j and ρ_1 (the pseudodensity of dissolved thymol) were assumed to be temperature dependent: ρ_1 was correlated with temperature according to eq 1 while for A_j the following equation was adopted:

$$A_j = \alpha_{1j}/(T/\text{K}) + \alpha_{2j} + \alpha_{3j}(T/\text{K}) \quad (6)$$

The adjustable constants were obtained by the least-squares method by fitting equations 1, 5, and 6 to the entire set of densimetry experimental data and are included in Table 5. With these parameters the mixture densities can be reproduced with a standard deviation of 0.000 12 g·cm⁻³.

Subsequently, excess molar volumes were calculated for mixtures with different contents of thymol, from pure 1,8-cineole up to saturation concentrations, as shown in Figure 2. Over this range of composition and at all the temperatures studied the excess molar volumes are negative with a minimum near $x_1 = 0.55$, and become more negative as the temperature increases. Since the molecular sizes of thymol and 1,8-cineole are of about the same order of magnitude, the obtention of negative values indicates the existence of hydrogen-bond interactions. The variation of the excess molar volume with temperature shows that raising the temperature results in an increase in these interactions.

The binary kinematic viscosity data were correlated by using the cubic equation of McAllister (12)

$$\ln \nu_m = x_1^3 \ln \nu_1 + 3x_1^2(1-x_1) \ln \nu_{12} + 3x_1(1-x_1)^2 \ln \nu_{21} + (1-x_1)^3 \ln \nu_2 + R^\circ \quad (7)$$

where R° is defined as

$$R^\circ = -\ln\left(x_1 + (1-x_1)\frac{M_2}{M_1}\right) + 3x_1^2(1-x_1) \ln\left(\frac{2}{3} + \frac{M_1}{3M_2}\right) + 3x_1(1-x_1)^2 \ln\left(\frac{1}{3} + \frac{2M_2}{3M_1}\right) + (1-x_1)^3 \ln\left(\frac{M_2}{M_1}\right) \quad (8)$$

x_1 being the mole fraction of thymol and M_1 and M_2 the

molecular masses of both components. The kinematic viscosities of the mixture and of pure thymol and 1,8-cineole are represented, respectively, by ν_m , ν_1 , and ν_2 , while ν_{12} and ν_{21} are the pseudokinematic viscosities of the mixture in the McAllister method.

Pure-liquid kinematic viscosities of 1,8-cineole were calculated using eqs 1 and 2 while for the dissolved thymol ν_1 was considered as an adjustable parameter. For ν_1 as well as for the two pseudokinematic viscosities of the mixture, ν_{12} and ν_{21} , a temperature dependence of the same form was adopted:

$$\ln \nu_{ij} = A_{ij} + B_{ij}/T \quad (9)$$

Therefore, the six Andrade parameters were estimated by the method of least squares over the experimental viscosities obtained at 288.15, 293.15, and 298.15 K (Table 6). In this narrow range of temperatures the McAllister method describes the kinematic viscosities with a standard deviation of $0.68 \times 10^{-6} \text{ m}^2\text{-s}^{-1}$, and consequently, the absolute viscosities are described with a standard deviation of 0.67 mPa·s. Including in the regression the viscosities measured at lower temperatures increases the error associated with the McAllister method (from 3 to 10%) which can be due to the large supercooling of most of the samples.

The dependence of the absolute viscosity on composition and temperature plotted in Figure 3 shows a maximum at x_1

= 0.65, thus reinforcing the hypothesis of the existence of specific interactions between the thymol and 1,8-cineole molecules.

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