

Densities, Viscosities, and Excess Molar Enthalpies of Binary Mixtures Containing Essential Oils at (298.15 and 313.15) K. The (S)-(-)-Limonene + Cineole, (S)-(-)-Limonene + Linalool, and Cineole + Linalool Systems

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Densities, ρ , viscosities, η , and excess molar enthalpies, H_m^E , of binary mixtures containing (S)-(-)-limonene [(-)-1-methyl-4-(1-methylethenyl)cyclohexene] + 1,8-cineole (1,3,3-trimethyl-2-oxabicyclo[2,2,2]-octane), (S)-(-)-limonene + linalool (3,7-dimethyl-1,6-octadien-3-ol), and cineole + linalool were determined at (298.15 and 313.15) K and at atmospheric pressure using a digital density meter, a Schott measuring system, and a flow microcalorimeter, respectively. The excess molar volumes, V_m^E , the viscosity deviations, $\Delta\eta$, and the H_m^E 's were calculated from experimental measurements. Results were fitted to the Redlich–Kister polynomial to obtain the adjustable parameters and standard deviations. Results were also qualitatively explained in terms of molecular interactions.

Introduction

Components of essential oils, such as (S)-(-)-limonene, cineole, and linalool, are used in several pharmaceuticals and in perfume industries.^{1,2} (S)-(-)-Limonene is the principal compound of citrus oil and makes up ≈ 90 mass % of citrus oil but does not contribute much to the flavor or fragrance of citrus oil while cineole, whose presence is ≈ 1 mass %, is an important oxygenated compound which makes the characteristic flavor and fragrance of citrus oil. Cineole and tymol are the two main components of tyme oil. Essential oils are conventionally processed by distillation or solvent extraction, resulting in the thermal degradation of some valuable components. The use of supercritical fluids is an alternative to conventional distillation processes, and the literature reports some papers about them^{3–6} but no study of the viscosity and excess properties of their binary mixtures is available. In this paper we report experimental data of kinematic viscosities, ν , densities, ρ , and excess molar enthalpies, H_m^E , of mixtures containing (S)-(-)-limonene + cineole, (S)-(-)-limonene + linalool, and cineole + linalool at (298.15 and 313.15) K with the purpose to provide new information about these mixtures, to correlate the experimental data, and to give a qualitative interpretation in terms of molecular interactions.

Experimental Section

Materials. (S)-(-)-Limonene (purity > 97%) was a Fluka product while cineole and linalool (purity 99% and 97%, respectively) were from Aldrich. All chemicals were purified following the procedure described elsewhere,⁷ and the purities of the distillate were checked by using a

Hewlett-Packard gas chromatograph (model 5890) supplied with a HP (cross-linked 5% ME siloxane) capillary column.

The impurity contents were <0.1 mass % for limonene and 0.7 mass % for cineole and linalool.

Prior to use, pure liquids were degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy), kept in dark bottles, and dried over molecular sieves (Union Carbide, type 4A, 1/16 in. pellets). The measured values of densities, ρ , dynamic viscosity, η , and refractive indices, n_D , were compared with literature data^{2,7–9} and are presented in Table 1. Refractive indices, n_D , were determined by using an Abbe Refractometer (Officine Galileo, Florence, Italy) with an uncertainty of 0.0001 unit. The thermostat temperature was constant to ± 0.01 K.

Values of densities and refractive indices are comparable with those of the literature while a disagreement is noted in the cases of viscosities of pure liquids. Authors remark that the viscosity value of (S)-(-)-limonene reported by Riddick et al.⁸ refers to a paper of 1908,¹⁰ while that of cineole⁹ refers to the pure liquid not distilled. No literature data of viscosity are available for linalool.

Moreover, the discrepancy observed between our viscosity data and those of the literature may be due partially to the nature of the oil and to the purity of the compounds studied in this paper. In fact, the (S)-(-)-limonene samples by Fluka and by Aldrich, for instance, show different values of optical rotation $[\alpha]_D^{20}$, say -90 ± 5 and -94 ± 3 , respectively, which compare with our value -97 . Riddick⁸ reports $[\alpha]_D^{20} = -122.1$.

Density Measurements. Solutions of different compositions were prepared by mass in a 25 cm³ flask using a digital balance (Mettler, model AE 160, Switzerland) accurate to within ± 0.0001 g following the method described elsewhere.¹¹ Densities, ρ , of pure components and their binary mixtures were measured using a vibrating-tube densimeter (Anton Paar, model DM 60, Graz, Austria)

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Table 1. Comparison of Experimental Densities, ρ , Dynamic Viscosities, η , and Refractive Indices, n_D , of Pure Components with Literature Values

| compound | T/K | $\rho/g\cdot cm^{-3}$ | | $\eta/mPa\cdot s$ | | n_D | |
|------------------|--------|-----------------------|----------------------|-------------------|--------------------|-----------|---------------------|
| | | this work | lit. | this work | lit. | this work | lit. |
| (S)-(-)-limonene | 298.15 | 0.839 44 | 0.8418 ⁷ | 0.846 | 1.806 ⁸ | 1.4707 | 1.4707 ⁷ |
| | 298.15 | | 0.8348 ⁸ | | | | 1.4701 ⁸ |
| | 313.15 | 0.827 88 | 0.8304 ⁸ | 0.702 | n.a. | 1.4641 | 1.4643 ⁷ |
| cineole | 298.15 | 0.920 13 | 0.9192 ⁸ | 2.559 | 2.303 ⁹ | 1.4556 | 1.4555 ⁸ |
| | 298.15 | | 0.92029 ⁹ | | | | |
| | 298.15 | | 0.92009 ⁹ | | | | |
| | 313.15 | 0.907 22 | n.a. | 1.886 | n.a. | 1.4491 | n.a. |
| linalool | 295.15 | | | | | 1.4610 | 1.4606 ² |
| | 298.15 | 0.858 09 | n.a. | 4.464 | n.a. | 1.4603 | n.a. |
| | 313.15 | 0.845 43 | n.a. | 2.552 | n.a. | 1.4535 | n.a. |
| | | | | | | | |

Table 2. Excess Molar Volumes, V_m^E , for Binary Mixtures Containing Essential Oils

| x_1 | $V_m^E/cm^3\cdot mol^{-1}$ | x_1 | $V_m^E/cm^3\cdot mol^{-1}$ |
|---|----------------------------|--------|----------------------------|
| (S)-(-)-Limonene (1) + Cineole (2); $T/K = 298.15$ | | | |
| 0.0715 | 0.070 | 0.6401 | 0.209 |
| 0.1121 | 0.103 | 0.7336 | 0.172 |
| 0.2018 | 0.163 | 0.8226 | 0.124 |
| 0.3270 | 0.216 | 0.8648 | 0.100 |
| 0.4164 | 0.237 | 0.9499 | 0.037 |
| 0.5584 | 0.229 | | |
| $T/K = 313.15$ | | | |
| 0.0715 | 0.063 | 0.6401 | 0.198 |
| 0.1121 | 0.096 | 0.7336 | 0.162 |
| 0.2018 | 0.154 | 0.8226 | 0.117 |
| 0.3270 | 0.205 | 0.8648 | 0.091 |
| 0.4164 | 0.224 | 0.9499 | 0.029 |
| 0.5584 | 0.218 | | |
| (S)-(-)-Limonene (1) + Linalool (2); $T/K = 298.15$ | | | |
| 0.0422 | 0.035 | 0.5620 | 0.319 |
| 0.1332 | 0.104 | 0.6389 | 0.336 |
| 0.2273 | 0.167 | 0.7679 | 0.326 |
| 0.3523 | 0.237 | 0.8478 | 0.279 |
| 0.4816 | 0.295 | 0.9236 | 0.179 |
| $T/K = 313.15$ | | | |
| 0.0422 | 0.037 | 0.5620 | 0.398 |
| 0.1332 | 0.125 | 0.6389 | 0.415 |
| 0.2273 | 0.209 | 0.7679 | 0.398 |
| 0.3523 | 0.301 | 0.8478 | 0.336 |
| 0.4816 | 0.373 | 0.9236 | 0.221 |
| Cineole (1) + Linalool (2); $T/K = 298.15$ | | | |
| 0.0536 | -0.058 | 0.5620 | -0.319 |
| 0.1357 | -0.139 | 0.6809 | -0.287 |
| 0.2205 | -0.207 | 0.8027 | -0.212 |
| 0.3081 | -0.260 | 0.8783 | -0.144 |
| 0.4288 | -0.306 | 0.9599 | -0.049 |
| 0.6051 | -0.310 | | |
| $T/K = 313.15$ | | | |
| 0.0536 | -0.049 | 0.5620 | -0.288 |
| 0.1357 | -0.120 | 0.6809 | -0.258 |
| 0.2205 | -0.181 | 0.8027 | -0.194 |
| 0.3081 | -0.232 | 0.8783 | -0.127 |
| 0.4288 | -0.277 | 0.9599 | -0.045 |
| 0.6051 | -0.279 | | |

equipped with a measuring cell (Anton Paar, type 602) and two digital thermometers (Anton Paar, DT-25 and DT-40). The apparatus was calibrated with deionized doubly distilled water¹² and dry air.¹³ The temperature in the measuring cell was regulated to ± 0.01 K, using an external bath circulator (Heto, type 01 DBT 623, Birkerød, Denmark) accurate to within ± 0.005 K.

The uncertainty of density measurements was $\pm 1 \times 10^{-5}$ g \cdot cm⁻³, and the excess molar volumes, V_m^E , were uncertain to ± 0.003 cm³ \cdot mol⁻¹. Corrections were made for buoyancy.

Before measurements, the apparatus was checked by determining V_m^E using the test mixture benzene + cyclohexane at 298.15 K, and our results agree with those of the literature¹⁴ within 1%.

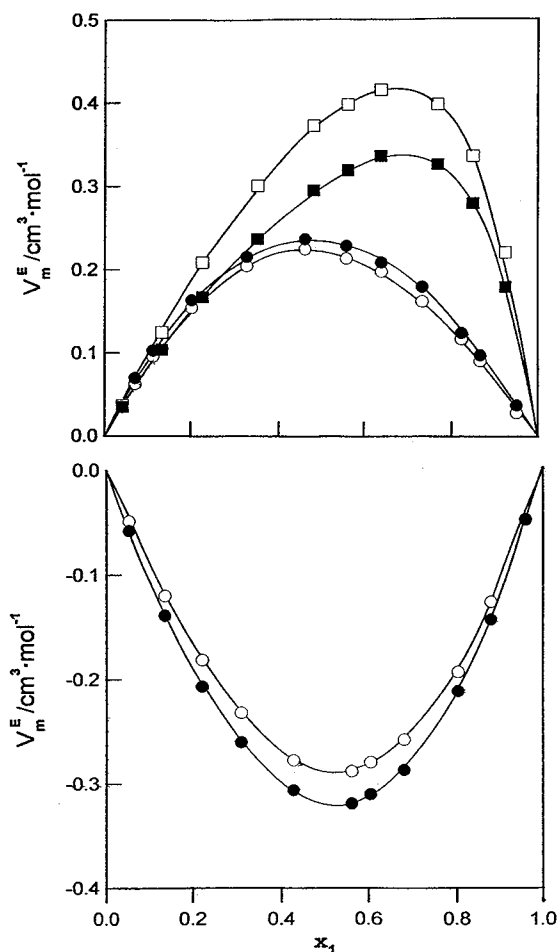


Figure 1. Excess molar volumes, V_m^E , versus the mole fraction, x_1 : upper part, (S)-(-)-limonene (1) + cineole (2) (●, ○) and (S)-(-)-limonene (1) + linalool (2) (■, □); closed points, at 298.15 K; open points, at 313.15 K; full lines, Redlich–Kister equation; lower part, cineole (1) + linalool (2) (●, ○); closed points, at 298.15 K; open point, at 313.15 K; full lines, Redlich–Kister equation.

Viscosity Measurements. Kinematic viscosities, ν , of pure liquids and mixtures were determined at (298.15 and 313.15) K using a Schott-Geräte (Mains, Germany) AVS 310 unit equipped with an Ubbelohde viscosimeter (capillary No. 0a) having a cell constant $k = 0.004 971$ mm² \cdot s⁻² and times varying from (180 to 1000) s. The experimental reproducibility between duplicate viscosity values of all samples was about $\pm 0.3\%$. The viscometer was calibrated with double-distilled water, whose viscosity is well-known and reported in the literature.⁸ The average of six flow times for each sample of liquid was taken for the purpose of the calculation of viscosity. A digital well-stirred water

Table 3. Experimental Densities, ρ , Dynamic Viscosities, η , and Deviations of Viscosities, $\Delta\eta$, of Binary Mixtures Containing Essential Oils

| x_1 | $\rho/\text{g}\cdot\text{cm}^{-3}$ | $\eta/\text{mPa}\cdot\text{s}$ | $\Delta\eta/\text{mPa}\cdot\text{s}$ | x_1 | $\rho/\text{g}\cdot\text{cm}^{-3}$ | $\eta/\text{mPa}\cdot\text{s}$ | $\Delta\eta/\text{mPa}\cdot\text{s}$ |
|---|------------------------------------|--------------------------------|--------------------------------------|--------|------------------------------------|--------------------------------|--------------------------------------|
| (S)-(-)-Limonene (1) + Cineole (2); $T/K = 298.15$ | | | | | | | |
| 0.0715 | 0.914 12 | 2.345 | -0.092 | 0.6401 | 0.867 72 | 1.162 | -0.300 |
| 0.1121 | 0.910 73 | 2.230 | -0.137 | 0.7336 | 0.860 25 | 1.050 | -0.252 |
| 0.2018 | 0.903 29 | 1.995 | -0.219 | 0.8226 | 0.853 16 | 0.963 | -0.187 |
| 0.3270 | 0.893 02 | 1.704 | -0.295 | 0.8648 | 0.849 00 | 0.928 | -0.149 |
| 0.4164 | 0.882 09 | 1.439 | -0.330 | 0.9499 | 0.843 04 | 0.872 | -0.060 |
| 0.5584 | 0.874 27 | 1.279 | -0.324 | | | | |
| $T/K = 313.15$ | | | | | | | |
| 0.0715 | 0.901 34 | 1.741 | -0.060 | 0.6401 | 0.855 70 | 0.929 | -0.199 |
| 0.1121 | 0.898 01 | 1.664 | -0.090 | 0.7336 | 0.848 33 | 0.851 | -0.167 |
| 0.2018 | 0.890 70 | 1.504 | -0.143 | 0.8226 | 0.841 34 | 0.785 | -0.127 |
| 0.3270 | 0.886 01 | 1.305 | -0.194 | 0.8648 | 0.838 03 | 0.759 | -0.103 |
| 0.4164 | 0.869 86 | 1.123 | -0.217 | 0.9499 | 0.831 37 | 0.716 | -0.046 |
| 0.5584 | 0.862 15 | 1.011 | -0.214 | | | | |
| (S)-(-)-Limonene (1) + Linalool (2); $T/K = 298.15$ | | | | | | | |
| 0.0422 | 0.857 21 | 4.062 | -0.249 | 0.5620 | 0.846 49 | 1.429 | -1.001 |
| 0.1332 | 0.855 32 | 3.237 | -0.745 | 0.6389 | 0.844 94 | 1.282 | -0.870 |
| 0.2273 | 0.853 37 | 2.695 | -0.947 | 0.7679 | 0.842 47 | 1.011 | -0.584 |
| 0.3523 | 0.850 79 | 2.072 | -1.118 | 0.8478 | 0.841 11 | 1.013 | -0.384 |
| 0.4816 | 0.848 12 | 1.626 | -1.096 | 0.9236 | 0.840 09 | 0.933 | -0.190 |
| $T/K = 313.15$ | | | | | | | |
| 0.0422 | 0.844 59 | 2.370 | -0.104 | 0.5620 | 0.834 09 | 1.086 | -0.427 |
| 0.1332 | 0.842 71 | 2.025 | -0.281 | 0.6389 | 0.832 623 | 0.998 | -0.372 |
| 0.2273 | 0.840 77 | 1.731 | -0.401 | 0.7679 | 0.830 33 | 0.877 | -0.255 |
| 0.3523 | 0.838 22 | 1.427 | -0.473 | 0.8478 | 0.829 13 | 0.814 | -0.170 |
| 0.4816 | 0.835 64 | 1.196 | -0.465 | 0.9236 | 0.828 26 | 0.755 | -0.088 |
| Cineole (1) + Linalool (2); $T/K = 298.15$ | | | | | | | |
| 0.0536 | 0.860 93 | 4.296 | -0.066 | 0.6050 | 0.895 94 | 3.019 | -0.293 |
| 0.1357 | 0.866 19 | 4.062 | -0.144 | 0.6809 | 0.900 68 | 2.900 | -0.267 |
| 0.2205 | 0.871 60 | 3.835 | -0.209 | 0.8027 | 0.908 18 | 2.740 | -0.195 |
| 0.3081 | 0.877 17 | 3.614 | -0.263 | 0.8783 | 0.912 79 | 2.660 | -0.131 |
| 0.4288 | 0.884 83 | 3.347 | -0.301 | 0.9599 | 0.917 70 | 2.591 | -0.045 |
| 0.5620 | 0.893 26 | 3.093 | -0.301 | | | | |
| $T/K = 313.15$ | | | | | | | |
| 0.0536 | 0.848 20 | 2.489 | -0.027 | 0.6050 | 0.882 94 | 2.023 | -0.126 |
| 0.1357 | 0.853 38 | 2.401 | -0.061 | 0.6809 | 0.887 67 | 1.983 | -0.115 |
| 0.2205 | 0.858 73 | 2.316 | -0.089 | 0.8027 | 0.895 21 | 1.933 | -0.085 |
| 0.3081 | 0.864 26 | 2.236 | -0.111 | 0.8783 | 0.899 82 | 1.910 | -0.573 |
| 0.4288 | 0.871 88 | 2.138 | -0.128 | 0.9599 | 0.904 79 | 1.892 | -0.021 |
| 0.5620 | 0.880 26 | 2.048 | -0.130 | | | | |

bath (Lauda, type E 200, Germany), whose temperature was controlled to ± 0.005 K, was used for all measurements.

Calorimetric Measurements. A flow microcalorimeter (LKB Producer, model 2107, Bromma, Sweden), driven by two automatic burets (ABU, Radiometer, Copenhagen, Denmark) necessary to pump pure liquids into the mixing cell of the apparatus, was used to determine the excess molar enthalpies, H_m^E , at (298.15 and 313.15) K and at atmospheric pressure. The calibration and operating procedure of the instrument was detailed previously.^{15,16} Mole fractions, x_1 , of limonene or cineole (component 1) were determined from flow rates with a precision of 1×10^{-4} , which lead to an error in H_m^E of (0.5–1) J·mol⁻¹.

The performance of the calorimeter was checked by measuring H_m^E over the whole composition for the test mixture cyclohexane + hexane at 298.15 K, and the agreement with literature results¹⁷ was <1%.

Results and Discussion

Tables 2 and 3 give the experimental results of the excess molar volumes, V_m^E , and dynamic viscosities, η , at (298.15 and 313.15) K while excess molar enthalpies, H_m^E , versus the mole fraction, x_1 , are reported in Table 4.

The plots of the V_m^E , deviation of viscosities, $\Delta\eta$, and H_m^E , versus the mole fraction, x_1 , are given in Figures 1–3.

The experimental density values, ρ , were used to calculate the excess molar volume, V_m^E , using the following equation

$$V_m^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \quad (1)$$

where ρ is the density of the mixture and M_1 , M_2 , x_1 , x_2 , ρ_1 , and ρ_2 are the molar weight, the mole fractions, and the densities of the pure compounds 1 and 2, respectively.

The deviations of viscosity, $\Delta\eta$, are obtained by the following equation

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \quad (2)$$

where η is the dynamic viscosity of the mixture and x_1 , x_2 , η_1 , and η_2 are the mole fractions and dynamic viscosities of components 1 and 2, respectively.

To each set of experimental values, a Redlich–Kister polynomial of the type

$$Q_m^E = x_1x_2 \sum_{k=0} a_k(x_1 - x_2)^k \quad (3)$$

has been fitted by an unweighted least-squares method, where $Q_m^E = V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$, $\Delta\eta/\text{mPa}\cdot\text{s}$, or $H_m^E/\text{J}\cdot\text{mol}^{-1}$, x_1 , and x_2 are the molar fractions of components 1 and 2,

Table 4. Excess Molar Enthalpies, H_m^E , for Binary Mixtures Containing Essential Oils

| x_1 | $H_m^E/\text{J}\cdot\text{mol}^{-1}$ | x_1 | $H_m^E/\text{J}\cdot\text{mol}^{-1}$ |
|---|--------------------------------------|--------|--------------------------------------|
| (S)-(-)-Limonene (1) + Cineole (2); $T/K = 298.15$ | | | |
| 0.0413 | 21 | 0.6739 | 59 |
| 0.0792 | 37 | 0.7561 | 27 |
| 0.1144 | 49 | 0.8052 | 8 |
| 0.1469 | 59 | 0.8611 | -9 |
| 0.2053 | 77 | 0.8921 | -15 |
| 0.2561 | 87 | 0.9254 | -18 |
| 0.3406 | 101 | 0.9612 | -14 |
| 0.4077 | 106 | 0.9697 | -12 |
| 0.5081 | 100 | 0.9800 | -9 |
| 0.6079 | 79 | | |
| $T/K = 313.15$ | | | |
| 0.0413 | 5 | 0.6079 | 22 |
| 0.0792 | 12 | 0.6739 | 1 |
| 0.1144 | 19 | 0.756 | -26 |
| 0.1469 | 26 | 0.8052 | -39 |
| 0.2053 | 38 | 0.8611 | -47 |
| 0.2561 | 48 | 0.8921 | -46 |
| 0.3406 | 57 | 0.9254 | -40 |
| 0.4077 | 59 | 0.9612 | -26 |
| 0.5081 | 46 | 0.9800 | -15 |
| (S)-(-)-Limonene (1) + Linalool (2); $T/K = 298.15$ | | | |
| 0.0441 | 82 | 0.6245 | 1049 |
| 0.0846 | 170 | 0.6891 | 1055 |
| 0.1217 | 261 | 0.7688 | 1021 |
| 0.1559 | 335 | 0.8160 | 944 |
| 0.2170 | 474 | 0.8693 | 799 |
| 0.2698 | 590 | 0.8987 | 691 |
| 0.3566 | 746 | 0.9301 | 536 |
| 0.4249 | 847 | 0.9638 | 306 |
| 0.5257 | 982 | | |
| $T/K = 313.15$ | | | |
| 0.441 | 100 | 0.6245 | 1111 |
| 0.846 | 192 | 0.6891 | 1101 |
| 0.1217 | 289 | 0.7688 | 1016 |
| 0.1559 | 388 | 0.8160 | 902 |
| 0.2170 | 537 | 0.8693 | 743 |
| 0.2698 | 660 | 0.8987 | 629 |
| 0.3566 | 837 | 0.9301 | 477 |
| 0.4249 | 950 | 0.9638 | 267 |
| 0.5257 | 1063 | | |
| Cineole (1) + Linalool (2); $T/K = 298.15$ | | | |
| 0.0428 | 6 | 0.6169 | 116 |
| 0.0821 | 15 | 0.6821 | 108 |
| 0.1183 | 23 | 0.7630 | 89 |
| 0.1517 | 35 | 0.8110 | 74 |
| 0.2115 | 53 | 0.8656 | 54 |
| 0.2634 | 70 | 0.8957 | 42 |
| 0.3492 | 94 | 0.9279 | 29 |
| 0.4169 | 108 | 0.9626 | 15 |
| 0.5176 | 119 | | |
| $T/K = 313.15$ | | | |
| 0.0428 | 6 | 0.6169 | 122 |
| 0.0821 | 14 | 0.6821 | 108 |
| 0.1183 | 24 | 0.7630 | 85 |
| 0.1517 | 36 | 0.8110 | 67 |
| 0.2115 | 54 | 0.8656 | 46 |
| 0.2634 | 70 | 0.8957 | 31 |
| 0.3492 | 99 | 0.9279 | 21 |
| 0.4169 | 114 | 0.9626 | 10 |
| 0.5176 | 127 | | |

respectively, and a_k 's are the adjustable parameters. The a_k values are given in Table 5 together with the standard deviation $\sigma(Q_m^E)$, defined as

$$\sigma(Q_m^E) = |\phi_{\min}|^{0.5} / (N - n) \quad (4)$$

In eq 4, N and n are the number of experimental points and of parameters, respectively, whereas ϕ_{\min} is the

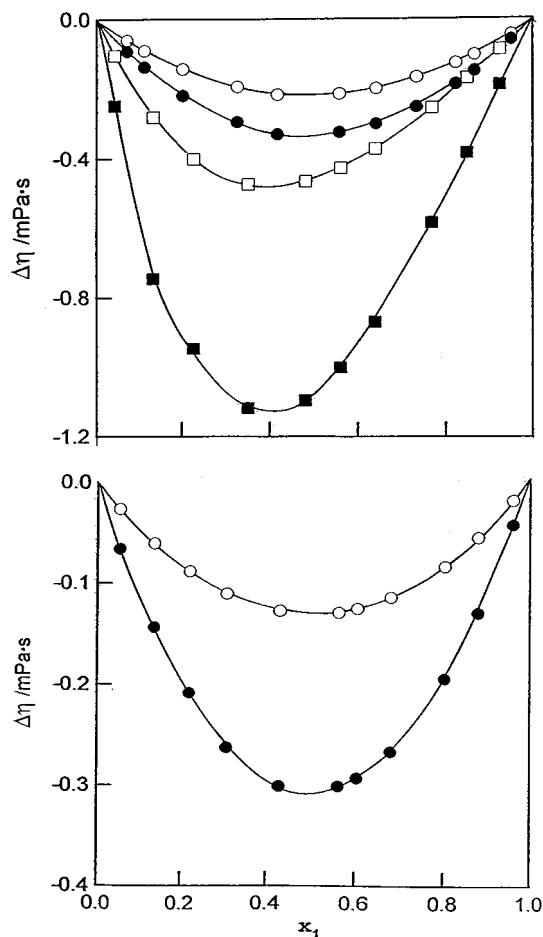


Figure 2. Deviation of viscosity, $\Delta\eta$, versus the mole fraction, x_1 : upper part, (S)-(-)-limonene (1) + cineole (2) (●, ○) and (S)-(-)-limonene (1) + linalool (2) (■, □); closed points, at 298.15 K; open points, at 313.15 K; full lines, Redlich–Kister equation; lower part, cineole (1) + linalool (2) (●, ○); closed points, at 298.15 K; open points, at 313.15 K; full line, Redlich–Kister equation.

minimum value of the objective function ϕ , defined as

$$\phi = \sum_{k=1}^N \omega_k^2 \quad (5)$$

where $\omega_k = Q_{m,\text{calcd}}^E - Q_m^E$; Q_m^E is the experimental value, and $Q_{m,\text{calcd}}^E$ is evaluated through eq 3.

Values of H_m^E are positive for the mixtures containing linalool whereas the mixture limonene + cineole shows an inversion of H_m^E as a function of mole fraction. Maxima of H_m^E range between (60 and 1100) $\text{J}\cdot\text{mol}^{-1}$, the lowest value being for limonene + cineole.

The temperature dependence of H_m^E is a small entity and shows no regular trend.

The systems containing linalool show a large increase of H_m^E in passing from cineole to limonene. This may be qualitatively explained by considering the approximated expression $H_m^E \approx E_{11} + E_{22} - 2E_{12}$, with E_{ij} the interaction energy between molecules i and j . The breakage of hydrogen bonds between the OH groups of linalool during mixing gives a large contribution to E_{22} , which is contrasted by the interaction energy E_{12} between the double bonds of linalool and the ethereal oxygen of cineole, which is absent in the mixture with limonene.

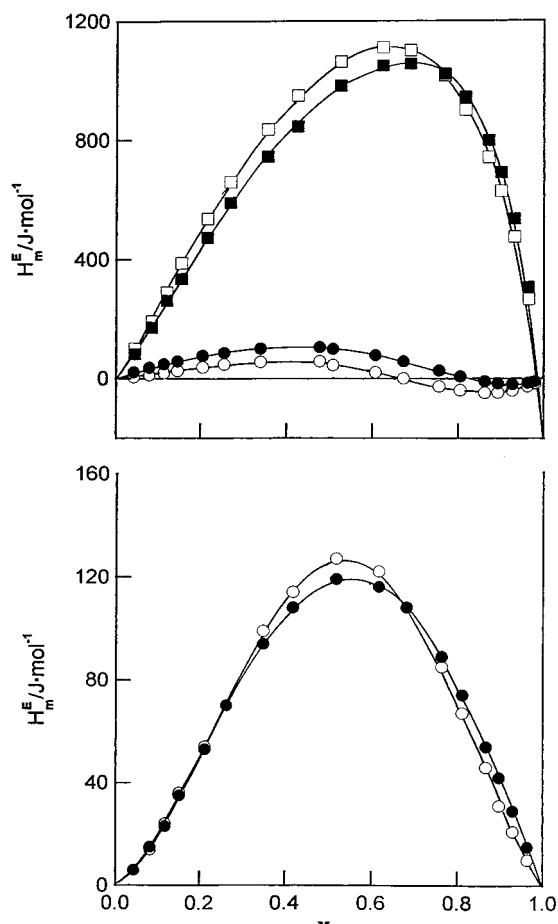


Figure 3. Excess molar enthalpies, H_m^E , versus the mole fraction, x_1 : upper part, (S)-(-)-limonene (1) + cineole (2) (●, ○) and (S)-(-)-limonene (1) + linalool (2) (■, □); closed points, at 298.15 K; open points, at 313.15 K; full line, Redlich–Kister equation; lower part, cineole (1) + linalool (2) (●, ○); closed points, at 298.15 K; open points, at 313.15 K; full line, Redlich–Kister equation.

Table 5. Least-Squares Parameters, a_k , Eq 3, and Standard Deviations, $\sigma(Q_m^E)$, Eq 4, of Binary Mixtures Containing Essential Oils

| function | a_0 | a_1 | a_2 | a_3 | $\sigma(Q_m^E)$ |
|---|---------|---------|---------|---------|-----------------|
| (S)-(-)-Limonene (1) + Cineole (2); $T/K = 298.15$ | | | | | |
| $V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$ | 0.9438 | -0.1173 | -0.0229 | -0.0348 | 0.0003 |
| $\Delta\eta/\text{mPa}\cdot\text{s}$ | -1.3217 | 0.0646 | | | 0.0003 |
| $H_m^E/\text{J}\cdot\text{mol}^{-1}$ | 404.8 | -228.3 | -387.5 | -305.0 | 0.6 |
| $T/K = 313.15$ | | | | | |
| $V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$ | 0.9000 | -0.1022 | -0.0702 | -0.0640 | 0.0023 |
| $\Delta\eta/\text{mPa}\cdot\text{s}$ | -0.8680 | 0.0178 | -0.0394 | | 0.0017 |
| $H_m^E/\text{J}\cdot\text{mol}^{-1}$ | 196.7 | -343.5 | -553.3 | -129.2 | 0.5 |
| (S)-(-)-Limonene (1) + Linalool (2); $T/K = 298.15$ | | | | | |
| $V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$ | 1.1997 | 0.7028 | 0.6870 | 0.3965 | 0.0015 |
| $\Delta\eta/\text{mPa}\cdot\text{s}$ | -4.3213 | 1.9612 | 0.0020 | | 0.0020 |
| $H_m^E/\text{J}\cdot\text{mol}^{-1}$ | 3797.0 | 2141.3 | 1754.4 | 1831.9 | 5.5 |
| $T/K = 313.15$ | | | | | |
| $V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$ | 1.5118 | 0.7813 | 0.7209 | 0.6470 | 0.0021 |
| $\Delta\eta/\text{mPa}\cdot\text{s}$ | -1.8315 | 0.7811 | -0.0681 | | 0.0013 |
| $H_m^E/\text{J}\cdot\text{mol}^{-1}$ | 4170.4 | 1999.0 | 938.8 | 1049.3 | 5.1 |
| Cineole (1) + Linalool (2); $T/K = 298.15$ | | | | | |
| $V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$ | -1.2699 | -0.1197 | | | 0.0018 |
| $\Delta\eta/\text{mPa}\cdot\text{s}$ | -1.2280 | 0.0006 | | | 0.0017 |
| $H_m^E/\text{J}\cdot\text{mol}^{-1}$ | 474.4 | 143.3 | -222.2 | | 0.7 |
| $T/K = 313.15$ | | | | | |
| $V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$ | -1.1519 | -0.1309 | 0.0752 | | 0.0016 |
| $\Delta\eta/\text{mPa}\cdot\text{s}$ | -0.5257 | -0.0110 | | | 0.0005 |
| $H_m^E/\text{J}\cdot\text{mol}^{-1}$ | 501.8 | 144.8 | -344.4 | -97.1 | 0.8 |

In fact, authors¹⁸ report the structure of an inclusion compound between limonene and a diol molecule, showing no specific interaction between the components.

Volumetric and viscometric determinations for mixtures containing linalool show the same trend as that for H_m^E . In fact, V_m^E is lower and $\Delta\eta$ is less negative for the mixture cineole + linalool, where the interaction energy E_{12} is relatively larger, since increasing interactions between different molecules are expected to show an increase in volume contraction and in the viscosity of the mixture.

Finally, $\Delta\eta$ is more temperature dependent than H_m^E and V_m^E ; thus, the viscosity of the mixture shows a decrease with increased temperature larger than that for the pure components.

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