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Excess molar enthalpies of binary mixtures containing pine resins in the range 288.15–313.15 K, and at atmospheric pressure
Use of the extended cell model of Prigogine

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Abstract

Excess molar enthalpies, H_m^E, of binary mixtures containing (*S*)-(−)-limonene + α-pinene, + β-pinene, or + *p*-cymene were determined using a flow microcalorimeter in the range 288.15–313.15 K, and at atmospheric pressure. The H_m^E are always positive, not exceeding 114 J mol^{-1}, and curves show a symmetrical trend. The temperature dependence of the calorimetric data is slight. Results were correlated to the Redlich–Kister polynomial and the adjustable parameters were determined by the least-squares method. Results were also interpreted by an extended modified cell model of Prigogine. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Enthalpies; Calorimeter; Correlation data; Cell model

1. Introduction

The main constituents of pine resins when steam distillation is applied to the liquid phase of pine resins are α-pinene, β-pinene, (*S*)-(−)-limonene, and *p*-cymene [1–3]. These components are used in many synthesis of a variety of chemicals, like synthetic resins and terpenic surfactants [4], in the pharmaceutical and cosmetic industries [5,6]. Particularly α-pinene proved to be exceptionally successful in the asymmetric reduction for synthesising optical pure materials via chiral organoboranes [7–9].

The purpose to need relevant thermodynamic data with the possibility of separating these components is evident: several papers concerning the use of supercritical fluids and vapour–liquid equilibrium data are found in the reference but no enthalpic data are available about.

The aim of this work is to provide comprehensive calorimetric measurements to obtain more informations on the interactions between molecules, to correlate the experimental data with the Redlich–Kister polynomial and to compare them with the values predicted by the Prigogine extended cell model [10].

2. Experimental

2.1. Chemicals

The (*S*)-(−)-limonene (purity > 97%) and α-pinene (purity > 99%) were Fluka products while β-pinene

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and *p*-cymene (both purity $> 99\%$) were from Aldrich.

All liquids were purified following the method described elsewhere [11].

The purities of the distillate were checked by means of a gas cromatograph (Hewlett-Packard, model 5890) using an HP (cross-linked 5% Me siloxane) capillary column with the result that the impurity contents were <1% mass for (*S*)-(−)-limonene, α-pinene, *p*-cymene, and <0.8% mass for β-pinene.

Purities of the liquids were also checked by comparing the measured densities, ρ, with those reported in [1,12] as shown in Table 1.

Densities, ρ, were determined using a vibrating tube densimeter (Anton Paar, model 60, Graz, Austria) equipped with a measuring cell (Type 602) whose operating procedure were described elsewhere [13].

Coefficients *A* and *B* for the temperature dependence of density of pure compounds

$$\rho = A + Bt\,(^\circ\mathrm{C}) \quad (1)$$

were also reported in Table 1.

Before measurements, all 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).

α-Pinene, as suggested by purchaser was stored in freezer at 4°C.

2.2. Calorimetric measurements

A flow microcalorimeter (LKB producer, AB, model 2107, Bromma, Sweden) equipped with two automatic burets (ABU, Radiometer, Copenhagen, Denmark) was used to determine the excess molar enthalpies. The calibration of the apparatus and the operating procedure were described elsewhere [14,15].

The temperature of the calorimeter was kept constant to ±0.01 K.

Mole fractions, x_1, of (*S*)-(−)-limonene (component 1) were determined from flow rates stated by the automatic burets and flow rates were selected to cover the entire mole fraction range.

The experimental uncertainties in H_m^E, and in mole fraction, x_1, were estimated to be <1% and 2×10^{-4}, respectively.

The performance of the calorimeter was checked by measuring H_m^E of the test mixture (cyclohexane+hexane). Agreement with reference results [16] was always <1%.

3. Correlation of the calorimetric data

Experimental H_m^E are listed in Table 2 and represented in Figs. 1 and 2.

Each set of experimental values was fitted to a Redlich–Kister polynomial of the type

$$H_m^E = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \quad (2)$$

where x_1, x_2 are the molar fractions of (*S*)-(−)-limonene and component 2.

The adjustable parameters a_k and the standard deviation $\sigma(H_m^E)$ are given in Table 3.

The polynomials of Eq. (2) were fitted to the results by the unweighed least-squares method.The standard

Table 1
Densities, ρ, of pure chemicals and comparison with reference data at 298.15 K[a]

Component	ρ (g cm^{-3})				
	Experiment	Reference	*A*	$10^4(-B)$ (°C)	$10^5\sigma(\rho)$
(*S*)-(−)-Limonene	0.83952	0.8418 [1] 0.8384 [12]	0.85909	7.83	3.4
α-Pinene	0.85390	0.8548 [1] 0.8539 [12]	0.87467	8.31	0.8
β-Pinene	0.86666	0.8655 [1] 0.8667 [12]	0.88475	7.48	7.6
p-Cymene	0.85288	0.8521 [1] 0.8533 [12]	0.87306	8.06	3.8

[a] Coefficients *A* and *B*, Eq. (1), and standard deviations $\sigma(\rho)$ in the range 288.15–313.15 K; correlation coefficient $|R| > 0.9995$.

Table 2
Excess molar enthalpies, H_m^E, of binary mixtures containing (*S*)-(−)-limonene + α-pinene, + β-pinene, or + *p*-cymene in the range 288.15–313.15 K

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
(*S*)-(−)-Limonene (1) + α-pinene (2)			
T = 288.15			
0.0393	12.0	0.5959	95.8
0.0757	24.1	0.6628	86.1
0.1094	34.3	0.7467	69.1
0.1407	44.5	0.7972	57.1
0.1972	58.1	0.8550	43.3
0.2467	69.6	0.8872	33.2
0.3295	85.5	0.9218	23.6
0.3957	95.0	0.9593	13.3
0.4956	99.8		
T = 298.15 K			
0.0393	9.7	0.5960	94.6
0.0757	19.7	0.6629	87.8
0.1094	27.8	0.7468	69.9
0.1408	39.6	0.7973	55.4
0.1973	55.9	0.8551	40.0
0.2468	67.1	0.8872	30.1
0.3296	85.1	0.9219	20.2
0.3959	94.4	0.9593	10.1
0.4957	101.3		
T = 303.15 K			
0.0394	10.1	0.5961	97.3
0.757	20.8	0.6629	89.8
0.1095	31.2	0.7468	72.5
0.1408	41.4	0.7973	62.9
0.1973	59.1	0.8551	48.4
0.2469	72.3	0.8872	38.8
0.3296	88.7	0.9219	28.5
0.3959	99.1	0.9594	15.6
0.4958	102.6		
T = 313.15 K			
0.0394	11.6	0.5962	108.6
0.758	22.0	0.6630	98.3
0.1095	35.7	0.7469	78.6
0.1409	45.9	0.7974	65.3
0.1974	64.3	0.8552	46.1
0.2469	77.1	0.8873	33.9
0.3297	98.3	0.9219	23.6
0.3960	108.8	0.9594	11.8
0.4959	114.6		
(*S*)-(−)-Limonene (1) + β-pinene (2)			
T = 288.15 K			
0.0388	6.3	0.5925	62.3
0.0747	12.5	0.6596	56.6
0.1080	19.7	0.7440	45.6
0.1390	25.0	0.7949	37.1
0.1950	34.5	0.8532	25.9
0.2441	43.6	0.8857	19.0

Table 2 (*Continued*)

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
0.3263	55.5	0.9208	12.1
0.3923	62.1	0.9588	6.6
0.4921	66.1		
T = 298.15 K			
0.0388	6.7	0.5924	64.9
0.0747	13.5	0.6596	57.1
0.1080	20.9	0.7440	47.2
0.1390	26.9	0.7949	37.7
0.1950	38.2	0.8532	26.3
0.2441	46.7	0.8857	19.5
0.3263	57.2	0.9208	12.5
0.3923	64.8	0.9588	6.4
0.4920	68.8		
T = 303.15 K			
0.0388	8.7	0.5925	71.2
0.747	16.6	0.6596	62.5
0.1080	24.2	0.7440	50.1
0.1390	31.5	0.7949	40.4
0.1950	42.4	0.8533	29.7
0.2441	52.1	0.8857	22.4
0.3264	63.2	0.9208	15.5
0.3924	68.5	0.9588	8.0
0.4921	73.1		
T = 313.15 K			
0.0388	6.9	0.5925	74.0
0.7470	14.2	0.6696	64.1
0.1080	21.6	0.7440	51.4
0.1390	28.6	0.7949	42.2
0.1950	41.7	0.8532	28.4
0.2441	50.4	0.8857	20.5
0.3263	65.2	0.9208	14.1
0.3923	73.6	0.9588	6.6
0.4921	79.6		
(*S*)-(−)-Limonene (1) + *p*-cymene (2)			
T = 288.15 K			
0.0388	15.1	0.5926	91.3
0.0747	27.0	0.6598	83.6
0.1081	38.7	0.7442	69.6
0.1391	47.0	0.7950	58.1
0.1951	61.2	0.8533	45.0
0.2442	72.1	0.8858	36.2
0.3265	86.5	0.9209	26.0
0.3925	93.1	0.9588	14.5
0.4923	96.6		
T = 298.15 K			
0.0388	9.9	0.5927	92.8
0.0748	19.9	0.6598	80.4
0.1081	27.8	0.7442	64.3
0.1391	38.9	0.7950	50.4
0.1951	54.3	0.8534	35.0
0.2443	67.0	0.8858	27.8
0.3265	84.1	0.9209	17.3

Table 2 (*Continued*)

x_1	H^E_m (J mol^{-1})	x_1	H^E_m (J mol^{-1})
0.3926	93.4	0.9588	8.3
0.4923	99.2		
$T = 301.15$ K			
0.0388	14.7	0.5927	98.8
0.0748	27.5	0.6598	86.6
0.1081	38.6	0.7442	68.5
0.1391	49.1	0.7951	54.0
0.1952	63.1	0.8534	38.6
0.2443	76.4	0.8858	27.6
0.3266	92.3	0.9209	17.8
0.3926	100.7	0.9588	8.3
0.4924	105.4		
$T = 313.15$ K			
0.0388	18.5	0.5928	106.9
0.0748	34.0	0.6596	98.6
0.1081	46.9	0.7443	81.2
0.1391	58.0	0.7951	69.0
0.1952	75.2	0.8534	51.4
0.2443	87.7	0.8858	40.9
0.3266	102.9	0.9209	29.6
0.3926	109.1	0.9588	16.5
0.4924	113.7		

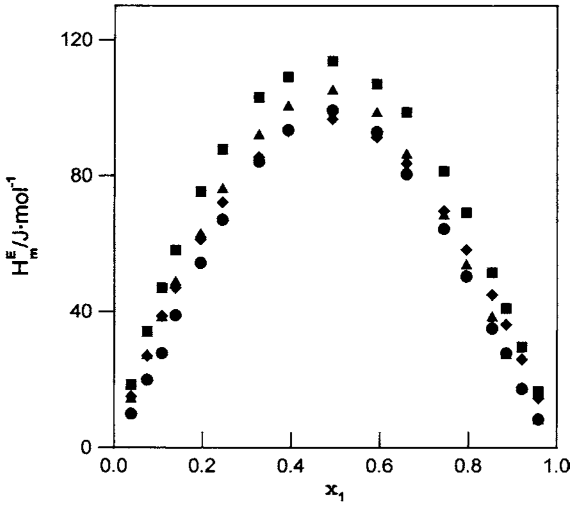

Fig. 2. Excess molar enthalpies, H^E_m, of binary mixtures containing (*S*)-(−)-limonene (1) + *p*-cymene (2). (◆, ●, ▲, ■) Refer at 288.15, 298.15, 303,15, and 313.15 K.

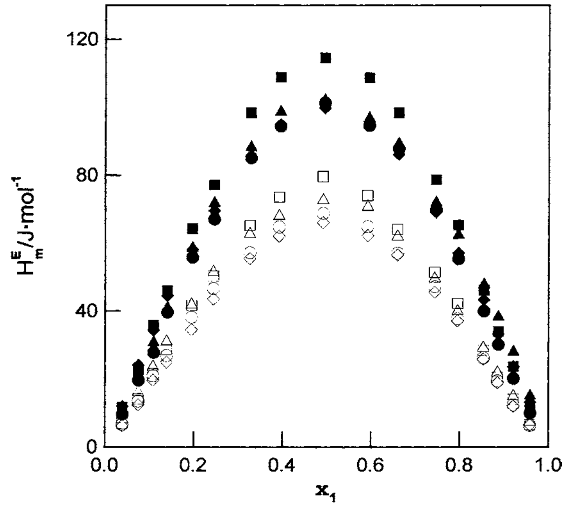

Fig. 1. Excess molar enthalpies, H^E_m, of binary mixtures containing (*S*)-(−)-limonene (1) + α-pinene, and + β-pinene (2). (◆, ●, ▲, ■) Refer at 288.15, 298.15, 303.15, and 313.15 K. Closed points refer to mixtures containing α-pinene, open points refer to mixtures containing β-pinene.

Table 3

Least-squares parameters, a_k, Eq. (2), and standard deviations, $\sigma(H^E_m)$, Eq. (3), of experimental excess molar enthalpies, H^E_m, of binary mixtures containing (*S*)-(−)-Limonene + α-pinene, + β-pinene, or + *p*-cymene in the range 288.15–313.15 K

T (K)	a_0	a_1	a_2	a_3	$\sigma(H^E_m)$ (J mol^{-1})
(*S*)-(−)-Limonene (1) + α-pinene (2)					
288.15	398.2	−10.3	−93.6		0.8
298.15	404.7	0.3	−166.1		0.9
303.15	411.6	−27.0	−89.9	114.7	0.6
313.15	460.7	−5.9	−173.8		0.9
(*S*)-(−)- (*S*)-(−)-Limonene					
288.15	264.8	−3.1	−114.4		0.5
298.15	274.3	−12.4	−113.3		0.7
303.15	293.6	−17.8	−90.9		0.7
313.15	314.6	−10.2	−161.7		0.6
(*S*)-(−)-Limonene (1) + *p*-cymene (2)					
288.15	380.9	−26.4			0.8
298.15	394.1	−30.2	−183.9		0.8
303.15	419.4	−39.9	−136.4	−68.5	0.7
313.15	450.8	−47.8			0.5

deviations, $\sigma(H_m^E)$, were calculated by means of the following equation

$$\sigma(H_m^E) = \left|\frac{\phi_{\min}}{N-n}\right|^{1/2} \tag{3}$$

where N and n are the number of experimental points and of adjustable parameters, whereas $\phi_{\min}$ is the minimum value of the objective function ϕ defined as

$$\phi = \sum_{k=1}^{N} \eta_k^2 \tag{4}$$

where $\eta_k = H_{m,\text{calcd}}^E - H_m^E; H_m^E$ is the experimental value and $H_{m,\text{calcd}}^E$ is evaluated through Eq. (2) and Table 3.

4. The cell model

We have used the model elaborated by Prigogine and co-workers [10,17,18], Salsburg and Kirkwood [19] and Rowlinson [20,21] to describe the mixtures studied in this paper which brings to the following formulas for H_m^E

$$H_m^E = x_1x_2E_{11}z\left[-1.44\theta + 10.76\left(\frac{RT}{zE_{11}}\right)^2 \times (-2\theta - \delta^2 + 4\delta\theta x_2 + 4x_1x_2\theta^2)\right] \tag{5}$$

$$\delta = \frac{E_{22} - E_{11}}{E_{11}} \tag{6}$$

$$\theta = \frac{E_{12} - (E_{11} + E_{22})/2}{E_{11}} \tag{7}$$

being z the number of nearest neighbours in the quasi-lattice model, E_{ij} the interaction energy between molecules i and j, and δ, θ normalised parameters. Values for z in the range 8–12 lead to a negligible variation of calculated parameters.

Table 4
Clausius–Clapeyron least-squares parameters C and D, Eq. (8), correlation coefficients $|R|$, and standard deviations $\sigma(P^o)$ for pure components

Component	C	D	$\|R\|$	$\sigma(P^o)$ (kPa)
(*S*)-(−)-Limonene	7.68707	−2503.68	0.9998	0.012
α-Pinene	7.36978	−2266.52	0.9999	0.011
β-Pinene	7.40698	−2330.52	0.9998	0.017
p-Cymene	7.70325	−2502.67	0.9998	0.016

Values of δ were calculated from Eq. (5) with E_{11} ad E_{22} determined from the heats of vaporisation λ of compounds.

The Clausius–Clapeyron equation

$$\log P^o = C + \frac{D}{T} \tag{8}$$

was used to obtain the heats of vaporisation, where $\lambda = -DR$, R being the gas constant. Constant C and D have been calculated by a least-square method and listed in Table 4 with the correlation coefficients $|R|$ and the standard deviations $\sigma(P^o)$.

Vapour pressure, P^o, of pure components have been determined using an equilibrium still (Fritz GmbH, Normag, Hofheim, Germany) whose operating procedure has been described elsewhere [22].

The values of the interaction energies, E_{ij}, as results of the cell model theory, are reported in Table 5 at the temperature of 298.15 K.

Figs. 3 and 4 show an example of comparison between the Redlich–Kister fit and the cell model trend for (*S*)-(−)-limonene + pinenes (Fig. 3), and + *p*-cymene (Fig. 4), at 298.15 K.

Similar behaviours were observed for other temperatures.

Table 5
Interaction energies, E_{ij}/J mol^{-1}, between molecules for binary mixtures containing (*S*)-(−)-limonene + α-pinene, +β-pinene, or + *p*-cymene, Eqs. (5)–(7), at 298.15 K

Mixture	E_{11}	E_{22}	E_{12}	$E_{11} + E_{22} - 2E_{12}$
(*S*)-(−)-Limonene (1) + α-pinene (2)	47.94	43.40	45.65	0.08
(*S*)-(−)-Limonene (1) + α-pinene (2)	47.94	44.61	46.25	0.05
(*S*)-(−)-Limonene (1) + *p*-cymene (2)	47.94	47.91	47.89	0.07

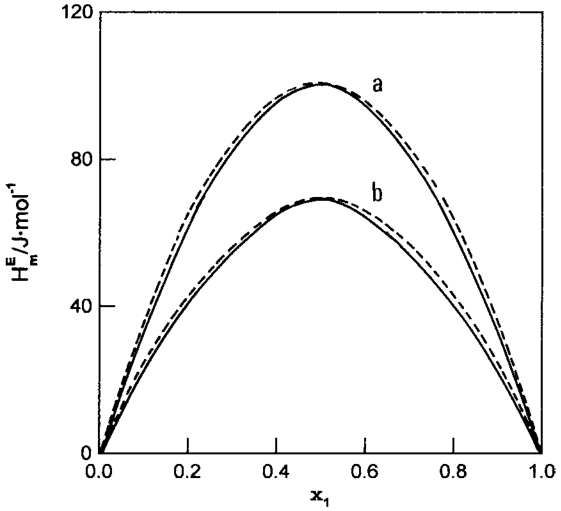

Fig. 3. Comparison between the Redlich–Kister fit (—) Eq. (2), and the cell model (- - -), Eq. (5). Curves a and b refer to the binary mixtures containing (*S*)-(−)-limonene (1) + α-pinene (2), or + β-pinene (2) at 298.15 K.

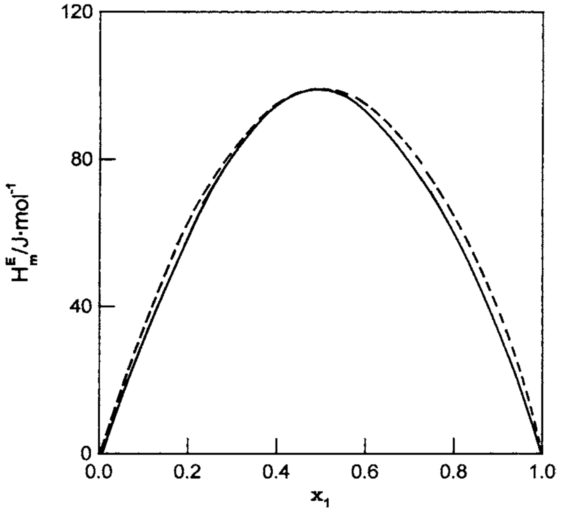

Fig. 4. Comparison between the Redlich–Kister fit (—) Eq. (2), and the cell model (- - -), Eq. (5) of the binary mixture containing (*S*)-(−)-limonene (1) + *p*-cymene (2), at 298.15 K.

5. Conclusions

As can be seen from Table 2 and Figs. 1 and 2, the values of H_m^E are always positive and small, not exceeding 114 J mol^{-1}, which allows application of the extended cell theory of Prigogine according to the model.

The interaction energies, E_{12}, obtained from the cell model (Table 5) are in the order *p*-cymene > *β*-pinene > α-pinene. The temperature dependence in the calorimetric data is positive but slight (in the order of 13–15 J mol^{-1}/25 K).

The behaviour of pinenes is the same observed in mixtures studied in previous works [23,24] where a qualitative explanation in terms of intermolecular forces is given.

As to the mixture containing *p*-cymene in the present work, we remark the following difference with respect to the mixtures of previous papers, though the H_m^E values of this note are too small for a significant comparison. In fact, the values of H_m^E for mixtures containing (*S*)-(−)-limonene + α-pinene and + *p*-cymene are almost coincident, while mixtures containing *p*-cymene in previous work showed values of H_m^E evidently smaller than the ones with α-pinene.

Most probably the (*S*)-(−)-limonene molecule finds a difficulty in the interactions with the π-electrons of *p*-cymene owing to its large dimension giving rise to an important steric effect.

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