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Excess molar enthalpies of binary mixtures containing phenetole + α-pinene or β-pinene in the range (288.15–313.15) K, and at atmospheric pressure Application of the extended cell model of Prigogine

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Abstract

Excess molar enthalpies, H_m^E, of binary mixtures containing phenetole (ethoxy benzene) + α-pinene, or β-pinene have been determined in the range (288.15–313.15) K, and at atmospheric pressure using a flow microcalorimeter. H_m^E curves are symmetrical with positive values over the entire concentration range and show higher values for the mixture containing α-pinene (the maximum value for H_m^E is 1072 J mol^{-1}). Only a slight influence of temperature on excess molar enthalpies has been observed for both systems. Experimental results have been correlated using the Redlich–Kister polynomial and the adjustable parameters have been evaluated by least-squares analysis. Results have also been interpreted by an extended modified cell model of Prigogine. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Calorimeter; Enthalpies; Correlation data; Cell model

1. Introduction

The present paper gives information about the excess molar enthalpies, H_m^E, of phenetole (ethoxy benzene) + α-pinene or β-pinene mixtures in the range (288.15–313.15) K and at atmospheric pressure.

Pinenes are used as potential solvents in extractive and azeotropic distillations, in the synthesis of a variety of chemicals and in perfume industries. The aim of the present study is to make a qualitatively interpretation of the interactions between the different types of molecules, to correlate the experimental data and to compare them with the values predicted by the Prigogine extended cell model [1]. To our knowledge, no enthalpic data are available in the literature for these systems.

2. Experimental

2.1. Chemicals

Phenetole, α-pinene, and β-pinene were from Aldrich with stated purities better than 99 mol% from purchaser. Liquids have been purified following the method described by Reich and Sanhueza [2] and the analyses of the products have been checked with the aid of a Hewlett–Packard gas chromatograph model

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Table 1
Densities, ρ, and refractive indices, n(D, 298.15 K) of pure chemicals and comparison with literature data at 298.15 K

Component	ρ (g cm^{-3})		n(D, 298.15 K)	
	Experimental	Literature	Experimental	Literature
Phenetole	0.96044	0.96049 [3]	1.5049	1.50485 [3]
α-Pinene	0.85391	0.8539 [3] 0.8548 [4]	1.4630	1.4632 [3] 1.4621 [4]
β-Pinene	0.86665	0.8667 [3] 0.8655 [4]	1.4767	1.4768 [3] 1.4748 [4]

5890 by using an HP (cross linked 5% Me siloxane) capillary column. After distillation, the obtained purities were ≥99.8 mol% for the three components. Before measurements, the pure liquids have been degassed by ultrasound (ultrasonic bath, type 460, Hellma, Milan, Italy), kept in dark bottles, and dried over molecular sieves (union Carbide, type 4A, 1/16 in pellets).

Densities, ρ, and refractive indices, n(D, 298.15 K), have been compared with literature values [3,4], and are given in Table 1. Densities and refractive indices have been determined using a digital density meter (Anton Paar, model DMA 60/602, Graz, Austria) and an Abbe refractometer (Carl Zeiss, Jena, Switzerland), respectively, both provided with temperature control by circulating thermostated water through it. Accuracies in densities and refractive indices have been estimated about 1×10^{-5} g cm^{-3} and 1×10^{-4} in all experiments.

The experimental data of densities, determined at atmospheric pressure have been fitted as a function of temperature, T (K), by means of the following equation:

$$\rho\,(\mathrm{g\,cm^{-3}}) = A + B(T\,(\mathrm{K}) - 273.15) \tag{1}$$

where coefficients A and B have been obtained by least-squares method and are shown in Table 2 with the correlation coefficients $|R|$ and S.D. $\sigma(\rho)$.

Table 2
Least-squares parameters A and B, Eq. (1), correlation coefficients $|R|$ and S.D. $\sigma(\rho)$ for pure components

Component	A	B	$\lvert R\rvert$	$\sigma(\rho)$ (10^5)
Phenetole	1.242142	−0.000945	0.9993	9.3
α-Pinene	1.101794	−0.000832	1.0002	0.8
β-Pinene	1.089125	−0.000748	0.9995	7.6

2.2. Calorimetric measurements

A microcalorimeter (LKB Producer AB, model 2107, Bromma, Sweden) operating under flow conditions has been used for measurements. Two automatic burets (ABU, Radiometer, Copenhagen, Denmark) necessary to pump pure liquids into the mixing cell of the calorimeter have been employed and mole fractions, x_1, of phenetole (component 1) have been determined from fluxes. The temperature of the apparatus has been kept constant to ±0.01 K through an external circulator bath maintained at a temperature about 10°C smaller than that of the calorimeter bath. Details of the equipment and its operating procedure have been described elsewere [5,6].

The reliability of the calorimeter has been checked by measuring the H_m^E for the hexane + cyclohexane test mixture, which agree within experimental errors (0.5%) with literature values [7].

The experimental uncertainties in H_m^E, and mole fractions, x_1, of phenetole have been estimated to be <1% and 2×10^{-4}, respectively.

3. Correlation of the calorimetric data

The measured excess molar enthalpies, H_m^E, are given in Table 3 and represented in Figs. 1 and 2. To each of the 12 sets of experimental values, a Redlich–Kister polynomial of the type

$$H_m^E = x_1x_2\sum_{k\geq0}a_k(x_1-x_2)^k \tag{2}$$

has been fitted by a method of unweighted least-squares, where x_1, x_2 are the molar fractions of phenetole and pinenes, and a_k are the adjustable

Table 3
Excess molar enthalpies H_m^E, of binary mixtures containing phenetole + α-pinene or β-pinene

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
Phenetole(1) + α-pinene(2)			
T = 288.15 K			
0.0496	225	0.6528	961
0.0945	397	0.7146	862
0.1354	523	0.7899	699
0.1727	642	0.8336	593
0.2385	786	0.8826	420
0.2946	897	0.9093	329
0.3852	1003	0.9376	235
0.4550	1053	0.9678	123
0.5561	1046		
T = 293.15 K			
0.0496	236	0.6528	940
0.0945	411	0.7148	855
0.1354	547	0.7899	685
0.1728	641	0.8337	556
0.2386	796	0.8826	425
0.2946	894	0.9093	317
0.3852	1006	0.9377	227
0.4551	1037	0.9678	119
0.5562	1027		
T = 298.15 K			
0.0497	228	0.6530	997
0.0946	398	0.7150	865
0.1356	531	0.7900	706
0.1729	631	0.8338	565
0.2387	789	0.8827	424
0.2948	905	0.9094	320
0.3854	1021	0.9377	220
0.4553	1073	0.9679	112
0.5564	1074		
T = 303.15 K			
0.0496	211	0.6528	940
0.0945	378	0.7148	849
0.1354	510	0.7899	676
0.1728	627	0.8337	553
0.2386	768	0.8826	408
0.2946	876	0.9093	318
0.3852	997	0.9377	222
0.4551	1042	0.9678	115
0.5562	1034		
T = 308.15 K			
0.0496	200	0.6528	940
0.0945	368	0.7148	834
0.1354	519	0.7899	668
0.1727	602	0.8337	552
0.2385	772	0.8826	405
0.2946	875	0.9093	320
0.3852	1006	0.9376	224
0.4550	1035	0.9678	118
0.5561	1026		
T = 313.15 K			
0.0496	191	0.6528	918
0.0945	349	0.7148	832
0.1354	480	0.7899	656
0.1727	590	0.8337	552
0.2385	752	0.8826	389
0.2946	861	0.9093	315
0.3852	994	0.9376	222
0.4550	1032	0.9678	116
0.5561	1019		
Phenetole(1) + β-pinene(2)			
T = 288.15 K			
0.0489	163	0.6495	788
0.0933	299	0.7118	702
0.1337	410	0.7875	559
0.1707	499	0.8317	466
0.2359	635	0.8811	338
0.2916	724	0.9081	273
0.3818	821	0.9368	192
0.4515	863	0.9674	101
0.5526	847		
T = 293.15 K			
0.0489	228	0.6495	780
0.0933	390	0.7118	700
0.1337	505	0.7875	563
0.1707	591	0.8317	474
0.2359	693	0.8811	336
0.2916	771	0.9081	257
0.3818	852	0.9368	180
0.4515	870	0.9674	93
0.5526	852		
T = 298.15 K			
0.0490	186	0.6497	806
0.0934	335	0.7120	754
0.1338	453	0.7876	651
0.1708	532	0.8317	567
0.2360	689	0.8812	446
0.2918	762	0.9081	379
0.3819	852	0.9368	275
0.4516	877	0.9674	153
0.5527	874		
T = 303.15 K			
0.0489	170	0.6495	800
0.0933	306	0.7118	708
0.1337	416	0.7874	577
0.1706	492	0.8316	473
0.2359	634	0.8811	347
0.2916	725	0.9081	265
0.3817	822	0.9368	187
0.4514	861	0.9674	97
0.5525	871		

Table 3 (*Continued*)

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
$T = 308.15$ K			
0.0489	165	0.6494	776
0.0932	301	0.7117	702
0.1337	411	0.7874	570
0.1706	498	0.8316	469
0.2358	630	0.8810	343
0.2915	726	0.9080	279
0.3816	820	0.9368	197
0.4513	855	0.9673	104
0.5525	847		
$T = 313.15$ K			
0.0489	155	0.6493	776
0.0932	285	0.7117	693
0.1336	388	0.7873	561
0.1705	488	0.8315	460
0.2357	624	0.8810	338
0.2914	713	0.9080	260
0.3815	809	0.9366	188
0.4512	854	0.9673	99
0.5523	843		

parameters. The a_k values are given in Table 4 together with the S.D. $\sigma(H_m^E)$ defined as

$$\sigma(H_m^E) = \left|\frac{\phi_{\min}}{(N-n)}\right|^{0.5} \tag{3}$$

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 4.

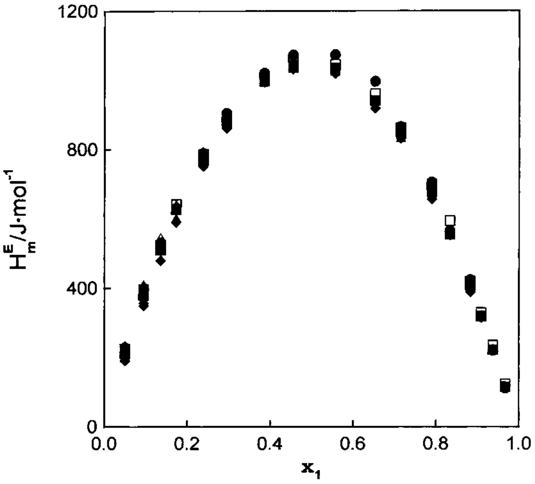

Fig. 1. Excess molar enthalpies H_m^E, of binary mixtures containing phenetole + α-pinene, (●, ■, ▲, ◆, △, □) refer at (288.15, 293.15, 298.15, 303.15, 308.15, and 313.15) K.

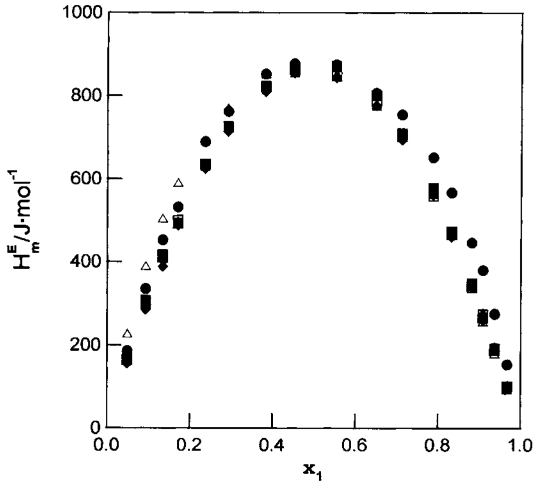

Fig. 2. Excess molar enthalpies, H_m^E, of binary mixtures containing phenetole + β-pinene, (●, ■, ▲, ◆, △, □) refer at (288.15, 293.15, 298.15, 303.15, 308.15, and 313.15) K.

Table 4

Least-squares parameters, a_k, Eq. (2), and standard deviations, $\sigma(H_m^E)$, Eq. (3), of experimental excess molar enthalpies, H_m^E, of binary mixtures containing phenetole + α-pinene or β-pinene at various temperatures

T (K)	a_0	a_1	a_2	a_3	$\sigma(H_m^E)$ (J mol^{-1})
Phenetole(1) + α-pinene(2)					
288.15	4238.2	35.1	176.4	−573.6	6.0
293.15	4180.7	−57.9	288.7	−686.7	6.3
298.15	4342.8	143.4	−111.5	−878.6	6.8
303.15	4194.7	−16.3	−58.9	−498.6	4.1
308.15	4185.4	−124.0	−121.2	−229.2	6.3
313.15	4155.1	−148.2	−309.5		5.4
Phenetole(1) + β-pinene(2)					
288.15	3471.6	−84.5	−108.7	−151.2	4.1
293.15	3478.0	−200.5	592.9	−1021.6	5.4
298.15	3514.8	−186.7	1004.0	782.5	5.8
303.15	3506.1	68.6	−123.0	−450.8	4.3
308.15	3445.8	−123.9			3.4
313.15	3443.6	−98.2	−218.7		4.6

4. The cell model

The model used to describe the system studied in this paper was elaborated by Prigogine and co-workers [1,8,9], Salsburg and Kirkwood [10] and Rowlinson [11,12] and brings to the following expression for H_{m}^{E}

$$H_{\mathrm{m}}^{E} = x_1 x_2 E_{11} z \left[-1.44\theta + 10.76 \left(\frac{RT}{zE_{11}} \right)^2 \times (-2\theta - \delta^2 + 4\delta\theta x_2 + 4x_1 x_2 \theta^2) \right] \quad (5)$$

$$\delta = \frac{E_{22} - E_{11}}{E_{11}} \quad (6)$$

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

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

Values of δ have been calculated from Eq. (5) with E_{11} and E_{22} evaluated from the heats of vaporization λ calculated from vapor–liquid measurements, using the Clausius–Clapeyron expression

$$\log P^{\mathrm{o}} = C + \frac{D}{T} \quad (8)$$

where $\lambda = -DR$, R being the gas constant. Constants C and D have been calculated by a least-square method and reported in Table 5 with the correlation coefficients $|R|$ and the standard deviations $\sigma(P^{\mathrm{o}})$.

Vapor pressure, P^{o}, of pure components have been determined using an equilibrium still (Fritz GmbH, Normag, Hofheim, Germany) the same as that used in previous papers [13–15] and its operating procedure has been described elsewere [16].

Table 5
Clausius–Clapeyron least-squares parameters C and D, Eq. (8), correlation coefficients $|R|$, and standard deviations $\sigma(P^{\mathrm{o}})$ for pure components

Component	C	D	$\|R\|$	$\sigma(P^{\mathrm{o}})$ (kPa)
Phenetole	7.718683	−2514.05	0.9995	0.039
α-Pinene	7.369784	−2266.52	0.9999	0.011
β-Pinene	7.406977	−2330.52	0.9998	0.017

Table 6
Interaction energies, E_{ij} (J mol^{-1}), between molecules for binary mixtures containing phenetole + α-pinene or β-pinene, Eqs. (5)–(7) at 298.15 K

Mixture	E_{11}	E_{22}	E_{12}	$E_{11} + E_{22}$ $-2E_{12}$
Phenetole(1) + α-pinene(2)	48.14	43.40	45.40	0.74
Phenetole(1) + β-pinene(2)	48.14	44.61	46.07	0.61

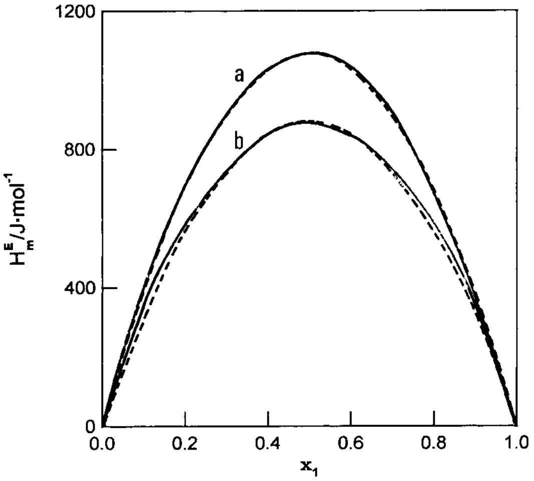

Fig. 3. Comparison between the Redlich–Kister fit (——) Eq. (2), and the cell model (- - -), Eq. (5). Curves a and b refer to mixtures containing α-pinene and β-pinene at 298.15 K.

Values of parameters (interaction energies) obtained by the cell model theory at the temperature of 298.15 K are reported in Table 6.

Fig. 3 shows, as an example, the comparison between the Redlich–Kister fit and the cell model curve for phenetole + α-pinene and β-pinene mixtures at 298.15 K. For mixtures at the other temperatures, similar discrepancies between best fit and calculated curve are observed.

5. Conclusions

Figs. 1 and 2 show large and positive values of H_{m}^{E} for all mixtures and only a slight influence of temperature on the thermal effect.

The large values of H_{m}^{E} indicate prevailing of breaking down of molecular bonds over bond formation after mixing. This result is due to interaction of π electrons in benzene ring with the OC_2H_5 group, leading to polarization of phenetole molecules and dipole–dipole interactions. Besides, values of H_m^E of mixtures containing α-pinene are higher than those in β-pinene.

This fact may be explained considering the two pinene molecules. The interaction energies E_{12} between the oxygen bond of phenetole and the double bond in the ring of α-pinene is partially hindered by the methyl group adjacent to the double bond, whereas in β-pinene the double bond is more available for the interaction with phenetole.

Table 6 collects values of E_{ii} and E_{12} obtained by the extended Prigogine model, and shows the resulting larger values of $H_m^E \propto E_{11} + E_{22} - 2E_{12}$ for the mixtures containing α-pinene.

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