

Figure 3. Eykman constant vs number of carbon atoms,  $N_c$ .

controlled to within  $\pm 0.01$  °C by circulating thermostated water through it. The resultant experimental error was estimated to be about  $\pm 0.0001$  for all experiments.

Densities were determined with a 10-mL Brand pycnometer that was calibrated with redistilled water at all the temperatures. The pycnometer was maintained in the bath until a constant meniscus level was obtained by removing the excess liquid when necessary. The samples were weighted in a Mettler Model AE100 balance with an accuracy of 0.0001 g. Replications of measured densities of the pure organic acids indicate an estimated precision of  $\pm 0.1$  kg m<sup>-3</sup>.

Acetic acid, propanoic acid, and valeric acid (p.a., Merck) and butanoic acid, hexanoic acid, heptanoic acid, octanoic acid, and oleic acid (BDH, minimum purity 99%) were used as supplied.

The water used for checking the pycnometer was redistilled and run through an ion-exchange column until it showed an electrical conductivity of  $< 1 \times 10^{-6}$   $\Omega^{-1}$  cm<sup>-1</sup>.

#### Analysis of Results

Refractive indices of pure organic acids are presented in Table I and have been plotted against temperature in Figure

1. In Table I are also indicated the parameters of eq 5, used

$$n_D = a + bt \quad (5)$$

to correlate the refractive indices as a function of temperature.  $dn/dt$  has a mean value of  $-3.8 \times 10^{-4}$  °C, which is in agreement with those predicted by some authors (3). The goodness of fit is higher than 0.999.

Densities were correlated in the same way, the parameters being presented in Table II. This includes the values of density in the temperature range from 20 to 50 °C.

In Figure 2, densities of pure organic acids are plotted against temperature.

The Eykman constant,  $K$ , is independent of temperature for all the acids that we have analyzed, the average deviation between the  $K$  values being smaller than  $\pm 0.0005$ . Figure 3 represents the variation of  $K$  versus the number of carbon atoms ( $N_c$ ) of the acid.

The values of refractive indices obtained by using the Lorentz-Lorenz equation (Table I) agree with the experimental ones within an average deviation of about  $\pm 0.0005$ .

#### List of Symbols

$a, b$	parameters of eq 5
$d$	density
$K$	Eykman constant (eq 1)
$n_D$	refractive index
$N_c$	number of carbon atoms of the acid
$R$	specific refractive index (eq 3)
$t$	temperature, °C

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## Densities and Refractive Indices of Components of Pine Resin

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Densities and refractive indices of  $\alpha$ -pinene,  $\beta$ -pinene, (S)-(-)-limonene, and *p*-cymene were measured in the temperature range 20–50 °C.

#### Introduction

Refractive index and density are physical properties of extreme importance in the characterization and identification of materials.

Components and derivatives of pine resin are used in the chemical and perfume industries.

As a part of a large work on the determination of vapor-liquid equilibrium of binary and multicomponent mixtures of components of pine resin (1, 2), the densities and the refractive indices of some of these compounds were measured at temperatures higher than ambient conditions.

#### Experimental Work

Refractive indices were measured between 20 and 50 °C

Table I. Densities and Refractive Indices of  $\alpha$ -Pinene at Several Temperatures

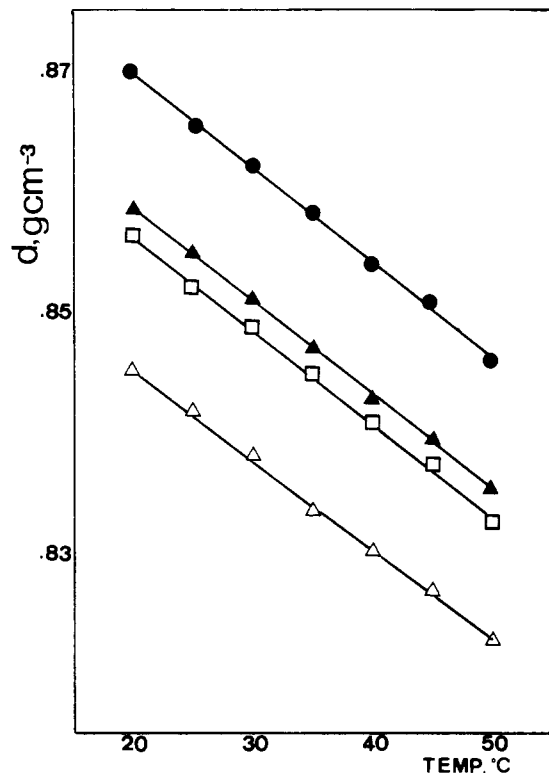
$t, ^\circ\text{C}$	$d, \text{g cm}^{-3}$				$n_D$			
	expt	ref 3	$a$	$10^4(-b), ^\circ\text{C}$	expt	ref 3	$c$	$10^4(-f), ^\circ\text{C}$
20	0.8585	0.8582	0.8734	7.71	1.4648	1.4659	1.4726	4.26
25	0.8548				1.4621			
30	0.8519				1.4603			
35	0.8469				1.4579			
40	0.8429				1.4558			
45	0.8394				1.4540			
50	0.8352				1.4518			

Table II. Densities and Refractive Indices of  $\beta$ -Pinene at Several Temperatures

$t, ^\circ\text{C}$	$d, \text{g cm}^{-3}$				$n_D$			
	expt	ref 3	$a$	$10^4(-b), ^\circ\text{C}$	expt	ref 3	$c$	$10^4(-f), ^\circ\text{C}$
20	0.8699	0.8654	0.8852	7.92	1.4772	1.4789	1.4849	4.21
25	0.8655				1.4748			
30	0.8621				1.4728			
35	0.8580				1.4705			
40	0.8538				1.4685			
45	0.8505				1.4660			
50	0.8459				1.4642			

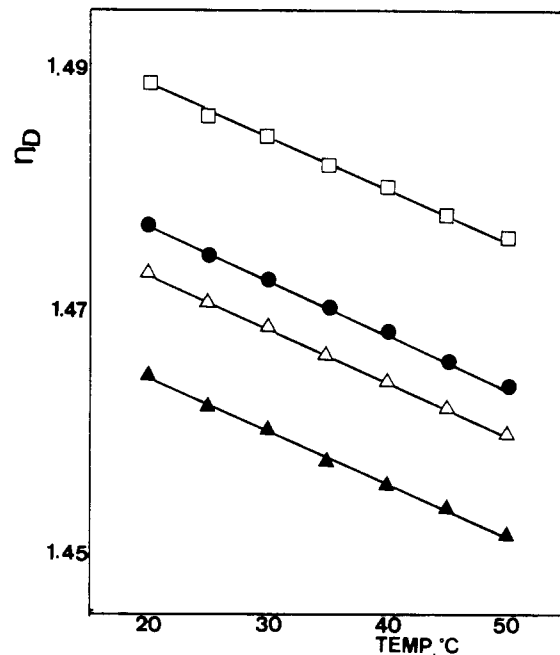
Table III. Densities and Refractive Indices of (*S*)-(-)-Limonene at Several Temperatures

$t, ^\circ\text{C}$	$d, \text{g cm}^{-3}$				$n_D$			
	expt	ref 3	$a$	$10^4(-b), ^\circ\text{C}$	expt	ref 3	$c$	$10^4(-f), ^\circ\text{C}$
20	0.8452	0.8411	0.8603	7.64	1.4732	1.4730	1.4809	4.21
25	0.8418				1.4707			
30	0.8382				1.4687			
35	0.8335				1.4665			
40	0.8304				1.4643			
45	0.8269				1.4622			
50	0.8226				1.4600			

Figure 1. Densities vs temperature for components of pine resin: (▲)  $\alpha$ -pinene; (●)  $\beta$ -pinene; (△) (*S*)-(-)-limonene; (□) *p*-cymene.

with a Krüss-Abbé refractometer provided with temperature control by circulating thermostated water through it. The resultant experimental error was estimated to be about  $\pm 0.0002$  for all experiments.

Densities were determined with a 10-mL Brand pycnometer that was calibrated with redistilled water at all the temperatures.

Figure 2. Refractive indices vs temperature for components of pine resin: (▲)  $\alpha$ -pinene; (●)  $\beta$ -pinene; (△) (*S*)-(-)-limonene; (□) *p*-cymene.

The pycnometer was maintained in the bath until a constant meniscus level was obtained by removing the excess liquid when necessary. The samples were weighed in a Mettler Model AE100 balance with an accuracy of 0.0001 g. Replications of measured densities of the pure components indicate an estimated precision of  $\pm 0.0001 \text{ g cm}^{-3}$ .

The  $\alpha$ -pinene (Fluka, >97%),  $\beta$ -pinene (Fluka, 80–90%), (*S*)-(-)-limonene (Fluka, >97%), and *p*-cymene (Fluka, >95%) were distilled. This fractionation was carried out in Vigreux columns, 1 m long and 2.5 cm in outside diameter. The purity

Table IV. Densities and Refractive Indices of *p*-Cymene at Several Temperatures

<i>t</i> , °C	<i>d</i> , g cm <sup>-3</sup>				<i>n<sub>D</sub></i>			
	expt	ref 3	<i>a</i>	10 <sup>4</sup> (- <i>b</i> ), °C	expt	ref 3	<i>c</i>	10 <sup>4</sup> (- <i>f</i> ), °C
20	0.8561	0.8573	0.8716	7.86	1.4891	1.4909	1.4969	4.21
25	0.8521				1.4865			
30	0.8486				1.4846			
35	0.8445				1.4824			
40	0.8406				1.4802			
45	0.8374				1.4782			
50	0.8326				1.4762			

of the distillate was checked by gas chromatography with use of a Perkin-Elmer chromatograph equipped with a flame ionization detector and a Shimadzu integrator. The impurities of the compounds were the other components. The impurity contents were less than 0.1% in  $\alpha$ -pinene and 0.15% in limonene and *p*-cymene. The purity of  $\beta$ -pinene was about 97%.

The water used for calibrating the pycnometer was redistilled and run through an ion-exchange column until it showed an electrical conductivity of  $<1 \times 10^{-8}$  mho cm<sup>-1</sup>.

### Analysis of Results

Densities were correlated with temperature as

$$d = a + bt \quad (1)$$

The average of the deviations between the calculated values obtained by using eq 1 and the experimental ones is  $3.4 \times 10^{-4}$  g cm<sup>-3</sup>, the maximum deviation being  $7.0 \times 10^{-4}$  g cm<sup>-3</sup>.

In Figure 1, densities of pure components are plotted against temperature.

The refractive indices were correlated in the same way:

$$n_D = c + ft \quad (2)$$

$dn_D/dt$  has a mean value of  $-4.23 \times 10^{-4}$  °C, which is in agreement with those predicted by some authors (3). The average of the deviations between the calculated values ob-

tained by using the eq 2 and the experimental ones is  $2.4 \times 10^{-4}$ , the maximum deviation being  $7.1 \times 10^{-4}$ .

Refractive indices of pure components are plotted against temperature in Figure 2.

In Tables I-IV are presented the values of densities and refractive indices for  $\alpha$ -pinene,  $\beta$ -pinene, limonene, and *p*-cymene, respectively.

### List of Symbols

<i>a, b</i>	parameters of eq 1
<i>c, f</i>	parameters of eq 2
<i>d</i>	density, g cm <sup>-3</sup>
<i>n<sub>D</sub></i>	refractive index
<i>t</i>	temperature, °C

Registry No.  $\alpha$ -Pinene, 80-56-8;  $\beta$ -pinene, 127-91-3; (-)-limonene, 5989-54-8; *p*-cymene, 99-87-6.

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## Viscosity and Density of Some Aliphatic, Cyclic, and Aromatic Hydrocarbons Binary Liquid Mixtures

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**Kinematic viscosities and densities of 68 linear, branched, cyclic and aromatic hydrocarbons binary liquid systems have been determined at 298.15 K over the entire composition range. The McAllister model has been used to fit experimental values of kinematic viscosities.**

### Introduction

Many chemical engineering designs require knowledge of liquid viscosities. The number of viscosity data published is relatively low. In the present work, viscosities and densities of 68 linear, branched, cyclic and aromatic hydrocarbon binary liquid mixtures have been measured at 298.15 K.

### Experimental Section

The pure hydrocarbons used are Fluka, "puriss" or "purum" quality, products (Table I). All the mixtures are prepared with a Model H-10W Mettler balance to  $\pm 0.5 \times 10^{-6}$  kg.

Pure components and liquid mixtures kinematic viscosities are determined with use of an automatic viscometer Lauda S thermostat bath equipped with two KPG Ubbelohde capillary viscometers of  $0.46 \times 10^{-3}$  and  $0.53 \times 10^{-3}$  m diameter, and two Ubbelohde microviscometers of  $0.40 \times 10^{-3}$  and  $0.53 \times 10^{-3}$  m diameter, all of them being calibrated with twice-distilled water. As many authors did (1-4), water has been used for calibration since it is the only product whose properties are known with good accuracy and is easily available with a high level of purity.