Densities and Refractive Indices of Pure Organic Acids as a Function of Temperature

Gabriela Bernardo-Gil,* Mercedes Esquível, and Albertina Ribeiro

Departamento Engenharia Química, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal

Densities and refractive indices of normal acids from acetic acid to octanoic acid were measured in the temperature range 20–50 °C. Densities and refractive indices of oleic acid were also measured at the same temperature range. The Eykman equation was used to check the accuracy of experimental densities and refractive indices. The refractive indices obtained by using the Lorentz–Lorenz equation agree with experimental ones within an average deviation of about ±0.0005.

Introduction

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

As a part of a complete work on the choice of solvents to extract organic acids, the densities and the refractive indices of some of these compounds were measured at temperatures higher than ambient conditions.

Both refractive index and density can be correlated, for each pure compound or mixture, by means of several empirical equations. In the present work, the Eykman and the Lorentz–Lorenz equations were used.

The Eykman equation (*1*)

$$\frac{n_D^2 - 1}{n_D + 0.4}\frac{1}{d} = K \qquad (1)$$

relates the refractive index n_D and the density d (both at the same temperature) by means the constant K. This constant was stated to be independent of temperature for the same compound.

Equation 1 can be expressed in the form

$$\frac{n_D^2 - 1}{d} = 0.4K + Kn \qquad (2)$$

The left-hand side of this equation is the Newton refraction. This expression states that the Newton refraction varies linearly as the first power of n_D.

The Lorentz–Lorenz equation

$$\frac{n_D^2 - 1}{n_D^2 + 2}\frac{1}{d} = R \qquad (3)$$

gives the specific refractive index R.

When written in the same form

$$\frac{n_D^2 - 1}{d} = 2R + Rn^2 \qquad (4)$$

states that the Newton refraction varies linearly as the second power of n_D.

Dreisbach (*1*) and Kurtz et al. (*2*) recommended the use of

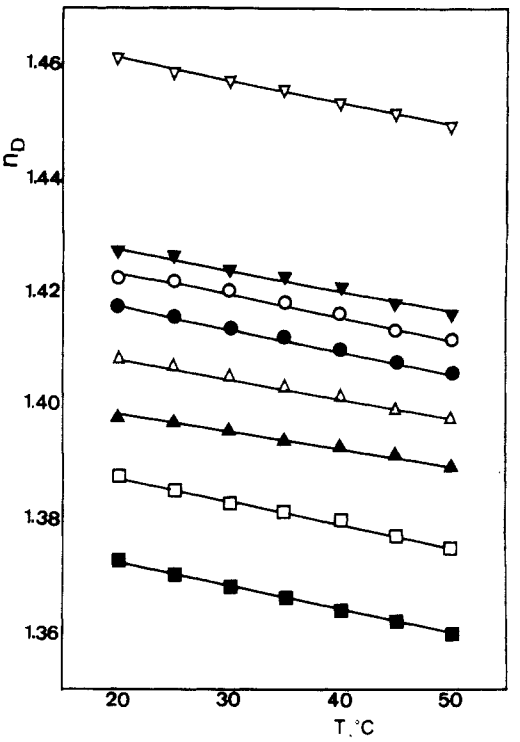

Figure 1. Refractive indexes vs temperature for organic acids: (■) acetic acid, (□) propanoic acid, (▲) butanoic acid, (△) valeric acid, (●) hexanoic acid, (○) heptanoic acid, (▼) octanoic acid, (▽) oleic acid.

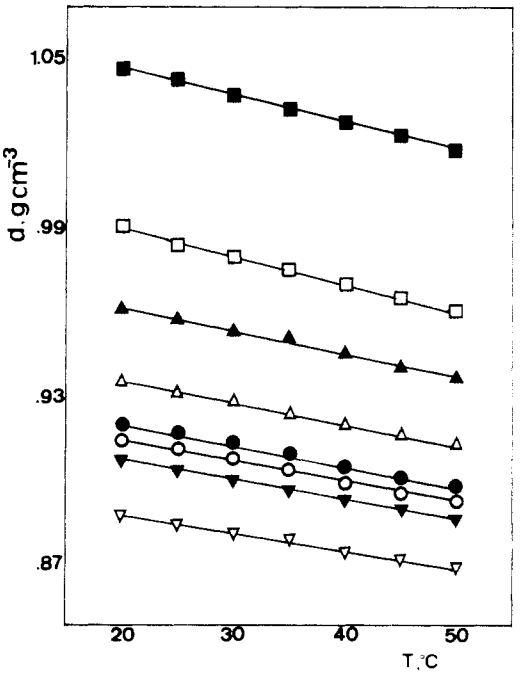

Figure 2. Densities vs temperature for organic acids: (■) acetic acid, (□) propanoic acid, (▲) butanoic acid, (△) valeric acid, (●) hexanoic acid, (○) heptanoic acid, (▼) octanoic acid, (▽) oleic acid.

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Table I. Refractive Indices of Organic Acids at Several Temperatures

t, °C	n expt	n lit.	n L-L eq[a]	$\bar{K}$	a	$10^4(-b)$, °C^{-1}
			Acetic Acid			
20	1.3730	1.3719[b]	1.3720	0.4745	1.3813	4.2
25	1.3707	1.3698[a]	1.3702			
30	1.3685		1.3683			
35	1.3666		1.3665			
40	1.3644		1.3697			
45	1.3624		1.3681			
50	1.3603		1.3610			
			Propanoic Acid			
20	1.3875	1.3865[b]	1.3874	0.5210	1.3954	4.1
25	1.3850	1.3848[c]	1.3852			
30	1.3830		1.3832			
35	1.3813		1.3811			
40	1.3790		1.3790			
45	1.3770		1.3768			
50	1.3751		1.3750			
			Butanoic Acid			
20	1.3978	1.3980[b]	1.3992	0.5522	1.4033	3.7
		1.3980[c]				
25	1.3963	1.3958[c]	1.3974			
30	1.3950		1.3954			
35	1.3938		1.3939			
40	1.3921		1.3916			
45	1.3909		1.3895			
50	1.3895		1.3880			
			Valeric Acid			
20	1.4080	1.4080[b]	1.4087	0.5798	1.4146	3.3
25	1.4062		1.4067			
30	1.4048		1.4049			
35	1.4030		1.4029			
40	1.4013		1.4009			
45	1.3998		1.3991			
50	1.3980		1.3972			
			Hexanoic Acid			
20	1.4170	1.4170[c]	1.4174	0.6019	1.4246	3.7
		1.4163[d]				
25	1.4156	1.4149[b,c]	1.4156			
30	1.4133	1.4132[c]	1.4140			
35	1.4118		1.4117			
40	1.4100		1.4094			
45	1.4079		1.4077			
50	1.4059		1.4058			
			Heptanoic Acid			
20	1.4230	1.4230[c]	1.4230	0.6120	1.4306	3.8
		1.4170[d]				
25	1.4212	1.4209[c]	1.4213			
30	1.4192	1.4192[c]	1.4195			
35	1.4174		1.4174			
40	1.4152		1.4154			
45	1.4134		1.4136			
50	1.4118		1.4118			
			Octanoic Acid			
20	1.4272	1.4279[b]	1.4281	0.6238	1.4347	3.6
		1.4280[c]				
25	1.4258	1.4260[c]	1.4257			
30	1.4240	1.4243[c]	1.4242			
35	1.4223		1.4220			
40	1.4204		1.4203			
45	1.4183		1.4182			
50	1.4166		1.4165			
			Oleic Acid			
20	1.4612	1.4599[b]	1.4607	0.6839	1.4688	3.9
		1.4582[c]				
25	1.4587		1.4586			
30	1.4570		1.4569			
35	1.4551		1.4551			
40	1.4532		1.4528			
45	1.4512		1.4514			
50	1.4491		1.4495			

[a] Lorentz-Lorenz equation. Values of n obtained by using eq 4. [b] Values obtained from ref 5. [c] Values obtained from ref 6. [d] Values obtained from ref 7.

the Eykman equation to check the accuracy of experimental data.

Table II. Densities of Organic Acids at Several Temperatures

t, °C	d, kg m^{-3} expt	d, kg m^{-3} ref 5[a]	a, kg m^{-3}	$10^4(-b)$, °C^{-1}
		Acetic Acid		
20	1048.9	1049.2	1067.6	9.326
25	1044.3			
30	1039.6			
35	1034.9			
40	1030.3			
45	1025.6			
50	1021.0			
		Propanoic Acid		
20	992.2	993.4	1010.8	9.405
25	987.2			
30	982.6			
35	977.8			
40	973.1			
45	968.1			
50	963.9			
		Butanoic Acid		
20	963.5	964.2*	979.6	8.044
25	959.5			
30	955.2			
35	952.1			
40	947.1			
45	942.7			
50	939.3			
		Valeric Acid		
20	938.2	939.2	953.9	7.853
25	934.0			
30	930.3			
35	926.3			
40	922.2			
45	918.6			
50	914.6			
		Hexanoic Acid		
20	921.6	922.3	932.5	7.600
25	918.0			
30	915.0			
35	910.6			
40	906.1			
45	902.7			
50	899.0			
		Heptanoic Acid		
20	917.6	918*	932.5	7.257
25	914.3			
30	910.9			
35	907.0			
40	903.2			
45	899.8			
50	896.2			
		Octanoic Acid		
20	910.6	910.6	924.0	7.000
25	906.1			
30	903.3			
35	899.2			
40	896.0			
45	892.2			
50	889.0			
		Oleic Acid		
20	890.1	890.6	902.5	6.221
25	886.6			
30	883.9			
35	880.7			
40	877.0			
45	874.7			
50	871.4			

[a] Values marked with an asterisk obtained from ref 4.

Experimental Work

Refractive indices were measured between 20 and 50 °C with a Krüss–Abbé refractometer provided with the temperature

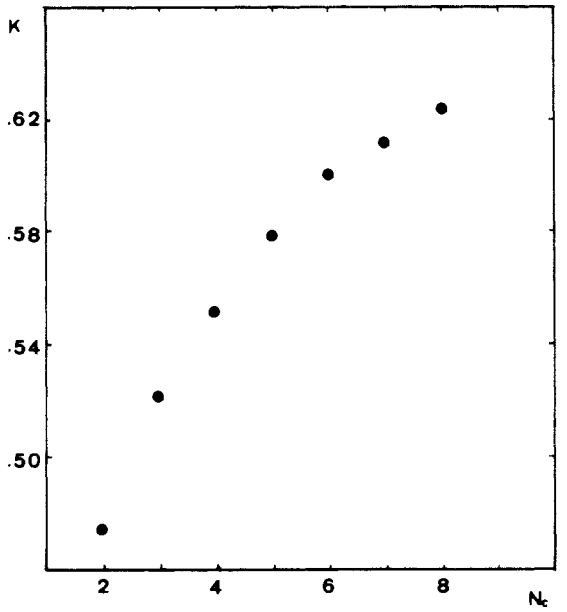

Figure 3. Eykman constant vs number of carbon atoms, N_c.

controlled to within ±0.01 °C by circulating thermostated water through it. The resultant experimental error was estimated to be about ±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 ±0.1 kg m^{-3}.

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 $<1 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$.

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 -3.8×10^{-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 ±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 ±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

Albertina Ribeiro and Gabriela Bernardo-Gil*

Departamento Engenharia Química, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal

Densities and refractive indices of α-pinene, β-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

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