Density and Viscosity Correlation for Several Common Fragrance and Flavor Esters

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The density and viscosity of several fragrance and flavor esters were measured over a temperature range of (293.15 to 343.15) K. The esters studied were ethyl formate, *cis*-3-hexenyl formate, ethyl acetate, butyl acetate, isoamyl acetate, hexyl acetate, *trans*-2-hexenyl acetate, *cis*-3-hexenyl acetate, ethyl propionate, ethyl butyrate, butyl butyrate, isoamyl butyrate, hexyl butyrate, *cis*-3-hexenyl isobutyrate, ethyl isovalerate, ethyl 2-methylbutyrate, and ethyl hexanoate. The experimental data were correlated by temperature-dependence equations.

Introduction

In the flavor and fragrance industries, aliphatic and acrylic esters are important materials in manufacturing processes.[1] Most of the esters used in the flavor and fragrance industries are acetates, and ethanol is the most common alcohol component. In addition to straight-chain saturated compounds, branched-chain compounds and unsaturated compound esters are also important.

Several studies of the thermodynamic behavior and physical properties of several ester compounds in binary mixtures have been performed.[1−4] However, detailed investigations of the physical properties of pure esters, especially their densities and viscosities over a wide range of temperature, are scarce in the literature. Therefore, this study was undertaken to obtain reliable density and viscosity data for a number of important flavor esters over a wide temperature range. The fragrance and flavor ester compounds chosen in this study with their physical characteristics are given in Table 1.

Experimental Section

Materials. High-purity and AR-grade samples of fragrance and flavor esters were purchased from Sigma-Aldrich Singapore. The purity of these chemicals was analyzed by gas chromatography (Shimadzu GC-17A) using a flame ionization detector with a DB-5 column. Helium (high purity) was used as the carrier gas. The purities of these esters are given in Table 1.

Density Measurements. Measurements of the densities of the pure components were carried out using a Mettler Toledo density meter type DE50 with an uncertainty of about 10^{-5} g·cm^{-3}. Prior to measurement, the instrument was calibrated with double-distilled water. The temperature of the measuring cell was maintained at various temperatures using a Julabo Thermostat model F12-MD with an uncertainty of 0.1 K.

Viscosity Measurements. For viscosity measurements, an automatic microviscosimeter (Anton Paar type AMV$_n$) equipped with an automatic timer (±0.01 s) was used. This instrument uses the rolling-ball principle according to DIN 53015 and ISO/DIS 12058, where a gold-covered steel ball rolls down inside an inclined, sample-filled glass capillary (diameter 0.16 cm). The uncertainty in time in the range of (0 to 250) s is less than 0.02 s with a resolution of ±0.01 s. The temperature range of this viscosimeter is (283.15 to 343.15) K with an uncertainty of less than 0.05 K. The instrument was periodically calibrated with double-distilled water. The uncertainty in the viscosity measurement was estimated to be better than 0.004 mPa·s. The measuring temperature was kept at the desired temperature by placing the sample-filled glass capillary in a block controlled with a Julabo refrigerating and heating circulator.

All measurements described above were performed at least three times, and the results were averaged to give the final values.

Experimental Results

The experimental results of the density and viscosity measurements of several fragrance and flavor ester compounds are given in Table 2. The density and viscosity of ethyl formate were measured only at 323.15 K, whereas for *trans*-2-hexenyl acetate and *cis*-3-hexenyl acetate the density and viscosity were measured only at 333.15 K because of the low boiling points of these esters. From this Table, it can be seen that the experimental values of the density and viscosity are generally in agreement with those from the literature.[1,4−10] However, for several viscosity data points, the deviation between experimental and literature data is as high as 0.04 mPa·s. This deviation is likely due to impurities in the flavor esters that we used.

The densities of pure esters were correlated using a temperature-dependence equation that has the following form:

$$\rho(T)/\mathrm{g\cdot cm^{-3}} = a + b(T/\mathrm{K}) + c(T/\mathrm{K})^2 \qquad (1)$$

Here, $\rho(T)$ is the density of the ester at absolute temperature and a, b, and c are fitted parameters. The fitted density parameters of each ester and standard deviation (σ) between experimental and calculated data are summarized in Table 3. Figure 1 depicts the experimental density data and predicted value versus temperature for several flavor esters. From Table 3 and Figure 1, it can be seen that eq 1 can predict the experimental data very well.

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Table 1. Physical Characteristics of the Esters Used in This Study[5]

name of ester	molecular formula	molecular weight/g·mol^{-1}	characteristic	purity/%	used
ethyl formate	$C_3H_6O_2$	74.08	clear liquid with a slightly pungent, fruity, ethereal odor	98.2	fruit flavors
cis-3-hexenyl formate	$C_7H_{12}O_2$	128.17	green-fruity odor, sweet	97.4	perfume and flavor to impart fruity-green notes
ethyl acetate	$C_4H_8O_2$	88.11	fruity-smelling liquid with a brandy note	99.6	fruit and brandy flavors
butyl acetate	$C_6H_{12}O_2$	116.16	liquid with a strong fruity odor	99.7	constituent of apple aroma
isoamyl acetate	$C_7H_{14}O_2$	130.19	strongly fruity-smelling liquid	98.9	banana flavors
hexyl acetate	$C_8H_{16}O_2$	144.21	liquid with a sweet-fruity, pearlike odor	99.0	fruit aroma composition
trans-2-hexenyl acetate	$C_8H_{14}O_2$	142.20	fresh-fruity, slightly green-smelling liquid	98.9	fruit flavors
cis-3-hexenyl acetate	$C_8H_{14}O_2$	142.20	fruit aromas and green tea	99.5	fruit flavors
ethyl propionate	$C_5H_{10}O_2$	102.13	liquid with fruity odor reminiscent of rum	99.4	creating both fruity and rum notes
ethyl butyrate	$C_6H_{12}O_2$	116.16	clear liquid with a fruity odor reminiscent of pineapples	99.6	perfume and flavor compositions
butyl butyrate	$C_8H_{16}O_2$	144.21	clear liquid with a sweet-fruity odor	99.3	fruit flavor composition
isoamyl butyrate	$C_9H_{18}O_2$	158.23	clear liquid with a very strong fruity odor	98.5	fruit flavors
hexyl butyrate	$C_{10}H_{20}O_2$	172.27	liquid with a very strong fruity odor	98.4	fruit flavor composition
cis-3-hexenyl isobutyrate	$C_{10}H_{18}O_2$	170.25	fruity-green odor	96.2	in perfume to create freshness in blossom compositions
ethyl isovalerate	$C_7H_{14}O_2$	130.19	colorless liquid with a fruity odor reminiscent of blueberries	98.8	fruity aroma composition
ethyl 2-methylbutyrate	$C_7H_{14}O_2$	130.19	liquid with a green-fruity odor reminiscent of apples	99.2	fruit flavor compositions
ethyl hexanoate	$C_8H_{16}O_2$	144.21	colorless liquid with a strong fruity odor reminiscent of pineapples	98.7	flowery-fruity notes in perfume compositions and fruit flavors

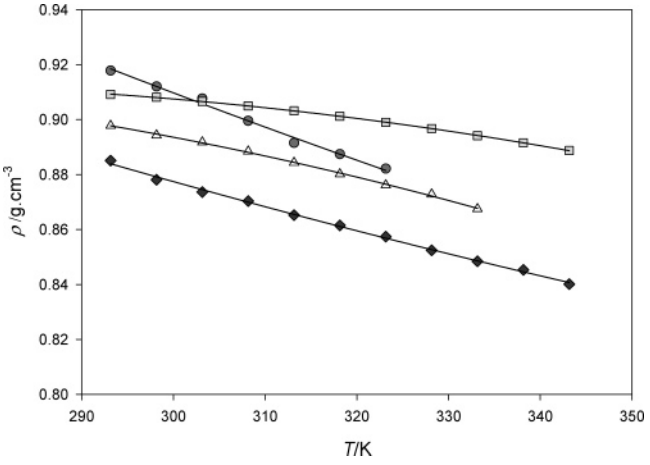

Figure 1. Experimental density data and correlated values for several flavor esters: ●, ethyl formate; ■, *cis*-3-hexenyl formate; ▲, *trans*-2-hexenyl acetate; ◆, *cis*-3-hexenyl isobutyrate.

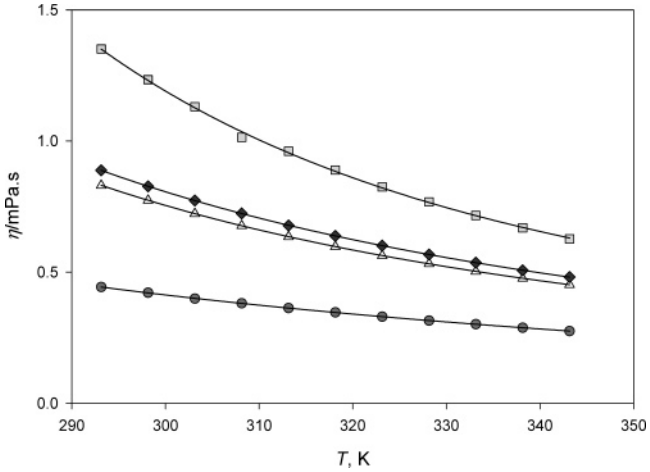

Figure 2. Experimental viscosity data and predicted values for several flavor esters: ●, ethyl acetate; ■, hexyl butyrate; ▲, ethyl 2-methylbutyrate; ◆, isoamyl acetate.

The viscosity of fragrance and flavor esters is a function of temperature and can be represented by the following equation

$$\log(\eta/\text{mPa·s}) = A + \frac{B}{T/\text{K}} + C(T/\text{K}) + D(T/\text{K})^2 \quad (2)$$

where A, B, C, and D are fitted parameters and η is the viscosity of pure esters in mPa·s. The fitted viscosity parameters of each ester and standard deviation (σ) between experimental and calculated data are summarized in Table 4. Figure 2 shows the experimental viscosity data and predicted value versus temperature for several flavor esters. Table 4 and Figure 2 reveal that eq 2 can also represent the experimental viscosity data very well.

Conclusions

New experimental density and viscosity data for several important flavor ester compounds over a wide range of temperature were obtained. The results were then correlated using temperature-dependence equations. It was found that the models used in this study represent the experimental data very well.

Table 2. Densities and Viscosity of Fragrance and Flavor Esters at Temperatures from (293.15 to 343.15) K

		ρ_l/g·cm^{-3}		η/mPa·s			ρ_l/g·cm^{-3}		η/mPa·s	
compounds	T/K	exptl	lit	exptl	lit	T/K	exptl	lit	exptl	lit
ethyl formate	293.15	0.91782	0.91680[5]	0.402		318.15	0.88741		0.314	
			0.92080[6]			323.15	0.88214	0.88390[6]	0.300	
	298.15	0.91206		0.381		328.15				
	303.15	0.90768	0.90760[6]	0.362		333.15				
	308.15	0.89954		0.345		343.15				
	313.15	0.89150	0.89360[6]	0.329						
cis-3-hexenyl formate	293.15	0.90915		0.599		323.15	0.89899		0.421	
	298.15	0.90813	0.90800[5]	0.561		328.15	0.89672		0.400	
	303.15	0.90660		0.527		333.15	0.89416		0.380	
	308.15	0.90495		0.496		338.15	0.89154		0.363	
	313.15	0.90317		0.469		343.15	0.88873		0.346	
	318.15	0.90119		0.443						
ethyl acetate	293.15	0.90048	0.90030[5]	0.443		323.15	0.87039		0.330	
	298.15	0.89481	0.89450[7]	0.421	0.424[4]	328.15	0.86713		0.315	
	303.15	0.88714		0.399	0.400[4]	333.15	0.86472		0.301	
	308.15	0.88221	0.88239[7]	0.381	0.385[4]	338.15	0.86141		0.288	
	313.15	0.87892		0.363		343.15	0.85836		0.275	
	318.15	0.87451		0.346						
butyl acetate	293.15	0.88104		0.732		323.15	0.85461		0.481	
	298.15	0.87645	0.87630[7]	0.677		328.15	0.85078		0.453	
	303.15	0.87130	0.87120[8]	0.628	0.631[8]	333.15	0.84792		0.428	
	308.15	0.86625	0.86620[7]	0.585		338.15	0.84439		0.405	
	313.15	0.86184		0.546		343.15	0.84177		0.384	
	318.15	0.85732		0.512						
isoamyl acetate	293.15	0.87824	0.86800−0.87800[5]	0.888		323.15	0.86431		0.601	
	298.15	0.87601		0.827		328.15	0.86014		0.567	
	303.15	0.87594		0.773		333.15	0.85798		0.536	
	308.15	0.87310		0.724		338.15	0.85405		0.507	
	313.15	0.87015		0.678		343.15	0.85107		0.481	
	318.15	0.86732		0.638						
hexyl acetate	293.15	0.87290	0.87310[1]	1.118	1.078[1]	323.15	0.84421		0.733	
			0.87260[9]							
	298.15	0.86730	0.86800[5]	1.036		328.15	0.83964		0.689	
	303.15	0.86260	0.86320[1]	0.962	0.982[1]	333.15	0.83515		0.649	
			0.86360[9]							
	308.15	0.85833		0.895		338.15	0.83140		0.612	
	313.15	0.85490	0.85350[1]	0.836		343.15	0.82630		0.579	
			0.85460[9]							
	318.15	0.84884		0.782						
trans-2-hexenyl acetate	293.15	0.89784	0.89800[5]	0.901		323.15	0.87614		0.582	
	298.15	0.89432		0.831		328.15	0.87281		0.547	
	303.15	0.89178		0.770		333.15	0.86749		0.514	
	308.15	0.88846		0.715		338.15				
	313.15	0.88435		0.666		343.15				
	318.15	0.88019		0.622						
cis-3-hexenyl acetate	293.15	0.90082		0.893		323.15	0.87789		0.576	
	298.15	0.89714		0.823		328.15	0.87521		0.542	
	303.15	0.89314		0.763		333.15	0.87143		0.509	
	308.15	0.89028		0.708		338.15				
	313.15	0.88619		0.660		343.15				
	318.15	0.88143		0.616						
ethyl propionate	293.15	0.89162	0.89170[5]	0.523		323.15	0.86433		0.378	
	298.15	0.88410		0.492		328.15	0.86089		0.360	
	303.15	0.87931	0.87887[8]	0.464	0.494[8]	333.15	0.85814		0.344	
	308.15	0.87412		0.441		338.15	0.85681		0.329	
	313.15	0.87061		0.418		343.15	0.85348		0.315	
	318.15	0.86734		0.398						
ethyl butyrate	293.15	0.87691	0.87850[5]	0.662		323.15	0.85843		0.465	
	298.15	0.87442	0.87347[10]	0.620		328.15	0.85444		0.442	
	303.15	0.87013		0.583		333.15	0.85389		0.420	
	308.15	0.86621		0.549		338.15	0.85132		0.400	
	313.15	0.86431		0.519		343.15	0.85004		0.382	
	318.15	0.86132		0.491						
butyl butyrate	293.15	0.87245	0.87090[5]	0.948		323.15	0.85147		0.618	
	298.15	0.86914		0.876		328.15	0.84801		0.581	
	303.15	0.86610		0.812		333.15	0.84622		0.548	
	308.15	0.86219		0.755		338.15	0.84403		0.517	
	313.15	0.85894		0.705		343.15	0.84147		0.486	
	318.15	0.85431		0.659						
isoamyl butyrate	293.15	0.86613	0.86510[5]	1.044		323.15	0.84578		0.686	
	298.15	0.86204		0.967		328.15	0.84231		0.646	
	303.15	0.85914		0.897		333.15	0.84073		0.609	
	308.15	0.85708		0.836		338.15	0.83545		0.575	
	313.15	0.85342		0.781		343.15	0.83276		0.545	
	318.15	0.85011		0.731						

Table 2 (Continued)

		ρ_L/g·cm^{-3}		η/mPa·s			ρ_L/g·cm^{-3}		η/mPa·s	
compounds	*T*/K	exptl	lit	exptl	lit	*T*/K	exptl	lit	exptl	lit
hexyl butyrate	293.15	0.86073	0.86520[5]	1.351		323.15	0.83078		0.825	
	298.15	0.85100		1.234		328.15	0.82819		0.768	
	303.15	0.84652		1.131		333.15	0.82677		0.716	
	308.15	0.84151		1.014		338.15	0.82381		0.669	
	313.15	0.83746		0.961		343.15	0.82076		0.627	
	318.15	0.83465		0.889						
cis-3-hexenyl isobutyrate	293.15	0.88508		1.024		323.15	0.85738		0.650	
	298.15	0.87812		0.941		328.15	0.85244		0.606	
	303.15	0.87361		0.868		333.15	0.84844		0.560	
	308.15	0.87034		0.804		338.15	0.84531		0.535	
	313.15	0.86522		0.741		343.15	0.84009		0.503	
	318.15	0.86149		0.690						
ethyl isovalerate	293.15	0.86623	0.86560[5]	0.805		323.15	0.84624		0.544	
	298.15	0.86401		0.752		328.15	0.84235		0.516	
	303.15	0.86012		0.703		333.15	0.84007		0.485	
	308.15	0.85598		0.659		338.15	0.83631		0.457	
	313.15	0.85179		0.620		343.15	0.83362		0.431	
	318.15	0.84739		0.581						
ethyl 2-methylbutyrate	293.15	0.86973		0.831		323.15	0.84674		0.563	
	298.15	0.86500	0.86890[5]	0.774		328.15	0.84159		0.532	
	303.15	0.86148		0.723		333.15	0.83841		0.503	
	308.15	0.85788		0.677		338.15	0.83548		0.476	
	313.15	0.85341		0.635		343.15	0.83146		0.452	
	318.15	0.84932		0.597						
ethyl hexanoate	293.15	0.87901	0.87100[5]	0.816		323.15	0.85642		0.541	
	298.15	0.87253		0.757		328.15	0.85193		0.509	
	303.15	0.86931		0.704		333.15	0.84788		0.482	
	308.15	0.86674		0.656		338.15	0.84532		0.456	
	313.15	0.86328		0.614		343.15	0.84146		0.429	
	318.15	0.86019		0.576						

Table 3. Parameters for the Density Correlation for the Fragrance and Flavor Esters

compounds	*a*	*b*	*c*	σ
ethyl formate	1.46554	-2.44133×10^{-3}	1.96192×10^{-6}	0.0041
cis-3-hexenyl formate	0.67480	1.83502×10^{-3}	-3.53118×10^{-6}	0.0006
ethyl acetate	1.99860	-6.24971×10^{-3}	8.53568×10^{-6}	0.0016
butyl acetate	1.69608	-4.48155×10^{-3}	5.80616×10^{-6}	0.0006
isoamyl acetate	0.59007	2.30538×10^{-3}	-4.50699×10^{-6}	0.0026
hexyl acetate	1.20940	-1.34331×10^{-3}	6.6227×10^{-7}	0.0011
trans-2-hexenyl acetate	0.74015	1.66995×10^{-3}	-3.86207×10^{-6}	0.0011
cis-3-hexenyl acetate	1.19615	-1.23970×10^{-3}	7.94135×10^{-7}	0.0016
ethyl propionate	1.97642	-6.25409×10^{-3}	8.69699×10^{-6}	0.0021
ethyl butyrate	1.47568	-3.31059×10^{-3}	4.33167×10^{-6}	0.0026
butyl butyrate	1.42365	-2.93727×10^{-3}	3.61375×10^{-6}	0.0021
isoamyl butyrate	0.95837	-1.78027×10^{-5}	-1.01675×10^{-6}	0.0026
hexyl butyrate	2.09934	-7.22490×10^{-3}	1.02082×10^{-5}	0.0021
cis-3-hexenyl isobutyrate	1.33005	-2.08366×10^{-3}	1.91639×10^{-6}	0.0016
ethyl isovalerate	1.31271	-2.24912×10^{-3}	2.48654×10^{-6}	0.0026
ethyl 2-methylbutyrate	1.23053	-1.63423×10^{-3}	1.37424×10^{-6}	0.0011
ethyl hexanoate	1.11638	-8.93011×10^{-4}	2.68015×10^{-7}	0.0016

Table 4. Parameters for Viscosity Correlation for the Fragrance and Flavor Esters

compounds	*a*	*b*	*c*	*d*	σ
ethyl formate	−5.06064	737.37681	0.01075	-1.16726×10^{-5}	0.0011
cis-3-hexenyl formate	−6.01904	954.74783	0.01202	-1.14524×10^{-5}	0.0006
ethyl acetate	−4.74308	659.9798 103	0.01145	-1.41899×10^{-5}	0.0006
butyl acetate	−5.49829	1000.90027	0.0086087	-6.69263×10^{-6}	0.0011
isoamyl acetate	−5.02068	865.50152	9.9597×10^{-3}	-1.05078×10^{-5}	0.0006
hexyl acetate	−4.40456	856.32033	7.3099×10^{-3}	-7.10792×10^{-6}	0.0006
trans-2-hexenyl acetate	−5.31784	976.68866	9.0022×10^{-3}	-8.12428×10^{-6}	0.0016
cis-3-hexenyl acetate	−5.33417	976.77772	9.0874×10^{-3}	-8.27495×10^{-6}	0.0006
ethyl propionate	−5.14522	806.15186	0.01028	-1.04632×10^{-5}	0.0011
ethyl butyrate	−5.17455	852.90821	0.01003	-9.94419×10^{-6}	0.0006
butyl butyrate	−7.18299	1161.06978	0.01531	-1.49862×10^{-5}	0.0006
isoamyl butyrate	−5.23957	959.94502	9.2246×10^{-3}	-8.38321×10^{-6}	0.0011
hexyl butyrate	−5.56517	1119.93544	8.0075×10^{-3}	-5.49352×10^{-6}	0.0011
cis-3-hexenyl isobutyrate	−5.36123	1021.97306	8.5427×10^{-3}	-7.19934×10^{-6}	0.0011
ethyl isovalerate	−4.72611	759.09741	0.01110	-1.41134×10^{-5}	0.0006
ethyl 2-methylbutyrate	−5.12216	884.82001	9.8046×10^{-3}	-9.89965×10^{-6}	0.0006
ethyl hexanoate	−6.42963	1054.49049	0.01315	-1.29215×10^{-5}	0.0011

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