[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

MIXED ESTERS OF LACTIC AND CARBONIC ACIDS. *n*-ALKYL CARBONATES OF METHYL AND BUTYL LACTATES, AND BUTYL CARBONATES OF *n*-ALKYL LACTATES

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The first paper of this series (1) described a group of esters made by acylating various esters of α-hydroxy acids with alkyl chloroformates. Several of these compounds were of special interest because their low volatility and their compatibility with various resins indicated that they might be useful as plasticizers. In a subsequent paper (2), which included some of the data presented in the present paper, additional carbonates of lactates were described, and their suitability as plasticizers for vinyl chloride polymers indicated. To facilitate a more systematic study of esters of this type, additional ones were prepared so that families of homologous compounds could be examined and various physical properties could be correlated with the number of carbon atoms in the compounds. Data on the use of these esters as plasticizers will be published elsewhere.

The compounds in the present study (Table I) fall into three series of homologs: (a) *n*-alkyl carbonates of methyl lactate, (b) *n*-alkyl carbonates of *n*-butyl lactate, and (c) *n*-butyl carbonates of *n*-alkyl lactates. The third series consists of five members, of which the butyl carbonates of methyl and butyl lactate are common to the first and second series, respectively. The members of the second and third series are isomeric and differ only in that their alkyl radicals are interchanged. As might be expected, the physical properties of the isomeric members of these two series are nearly identical. Since in most cases the differences are within or near the estimated experimental error, and all the relationships developed for the physical constants of the second series fit the third series almost as well, the two series are treated herein as one family.

Boiling points and vapor pressures. Figures 1 and 2 show the boiling points of the esters as a function of the pressure. The temperature scales are laid off as a linear function of $1/(t + 193)$, where t = °C. The usual form of the Cox chart, where the temperature scale is determined by $1/(t + 273)$ was unsatisfactory because the data fell on lines which were convex upward instead of straight. Charts whose scales were derived from $1/(t + 230)$ were better, but the curvature was still present. The scales determined by $1/(t + 193)$ gave straight lines, and charts having this scale were conveniently prepared from commercial Cox chart paper having a scale $1/(t + 273)$ by adding 80° to each temperature designated on the chart. The mathematical proof of this transformation will be published elsewhere (3). The boiling points of the butyl carbonates of alkyl lactates were generally within 1° of those of the isomeric alkyl carbonates of butyl lactate; hence, separate lines for them are not shown in Figure 2.

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TABLE I

n-ALKYL CARBONATES OF *n*-ALKYL LACTATES ROCOOCH(CH$_3$)COOR'

R	R'	YIELD, %	C		H		n_D^{20}	n_D^{40}	d_4^{20}	d_4^{40}	VISCOSITY, CPS.,		MOL. REFRACTION, 20°		SOLUBILITY IN WATER AT 25°, g./100 cc.
			Calc'd	Found	Calc'd	Found					20°	40°	Calc'd[a]	Found	
Methyl	Methyl[b]	58	44.5	44.5	6.2	6.4	1.4100	1.4020	1.1586	1.1363	5.42	2.90	34.86	34.68	4.07
Ethyl	"	34	47.7	47.9	6.9	7.1	1.4110	1.4035	1.1125	1.0913	4.78	2.63	39.48	39.32	1.65
Propyl	"	68	50.5	50.3	7.4	7.5	1.4163	1.4072	1.0820	1.0626	5.47	3.06	44.10	44.14	0.52
Butyl	"	61	52.9	52.6	7.9	7.9	1.4196	1.4112	1.0604	1.0411	5.99	3.26	48.71	48.64	.18
Amyl	"	41	55.0	55.2	8.3	8.5	1.4227	1.4150	1.0426	1.0231	7.30	3.78	53.33	53.26	.05
Hexyl	"	68	56.9	56.9	8.7	8.6	1.4255	1.4178	1.0229	1.0047	8.07	4.08	57.95	58.13	.01
Octyl	"	63	60.0	60.5	9.3	9.5	1.4304	1.4228	1.0010	0.9829	11.38	5.25	67.19	67.22	—
Decyl	"	66	62.5	62.7	9.8	9.7	1.4346	1.4273	0.9830	.9664	15.65	7.35	76.42	76.48	—
Methyl	Butyl	54	52.9	53.0	7.9	7.5	1.4170	1.4092	1.0575	1.0373	5.40	2.99	48.71	48.57	0.18
Ethyl	"	54	55.0	54.8	8.3	8.3	1.4181	1.4102	1.0325	1.0138	5.16	2.95	53.33	53.28	.07
Propyl	"	66	56.9	56.3	8.7	8.8	1.4218	1.4140	1.0189	0.9993	6.24	3.40	57.95	57.91	.01
Butyl	"	73	58.5	59.1	9.0	9.2	1.4240	1.4162	1.0049	.9864	6.51	3.64	62.57	62.55	—
Amyl	"	73	60.0	59.8	9.3	9.4	1.4263	1.4188	0.9943	.9763	7.49	3.90	67.19	67.13	—
Hexyl	"	65	61.3	61.3	9.6	9.7	1.4288	1.4212	.9823	.9647	8.96	4.64	71.80	71.97	—
Octyl	"	70	63.5	63.5	10.0	10.3	1.4332	1.4260	.9554	.9387	10.78	5.59	81.04	82.29	—
Decyl	"	66	65.4	65.4	10.4	10.8	1.4362	1.4290	.9551	.9391	15.19	7.46	90.28	90.51	—
Dodecyl	"	76	67.0	67.1	10.7	10.9	1.4394	1.4317	.9460	.9309	19.05	9.15	99.51	99.75	—
Butyl	Octyl	86	63.5	63.6	10.0	10.2	1.4324	1.4247	.9687	.9516	11.60	5.82	81.04	81.04	—
Butyl	Decyl	97	65.4	65.6	10.4	10.7	1.4358	1.4284	.9565	.9399	14.78	7.27	90.28	90.31	—
Butyl	Dodecyl	98	67.0	66.8	10.7	10.6	1.4390	1.4320	.9461	.9304	17.92	8.55	99.51	99.66	—

[a] Eisenlohr's constants were used because they gave slightly better agreement with observed values than did those of Vogel, *J. Chem. Soc.*, 1833 (1948). The two sets of constants gave the same calculated values for the compounds of highest molecular weight, but differed by 0.4 for the compounds of lowest molecular weight, Eisenlohr's being the higher. [b] This compound has been reported by Ritchie, *J. Chem. Soc.*, 1054 (1935).

Straight lines were obtained by plotting the logarithm of the vapor pressure of either family of esters, at any fixed temperature, *versus* the number of carbon

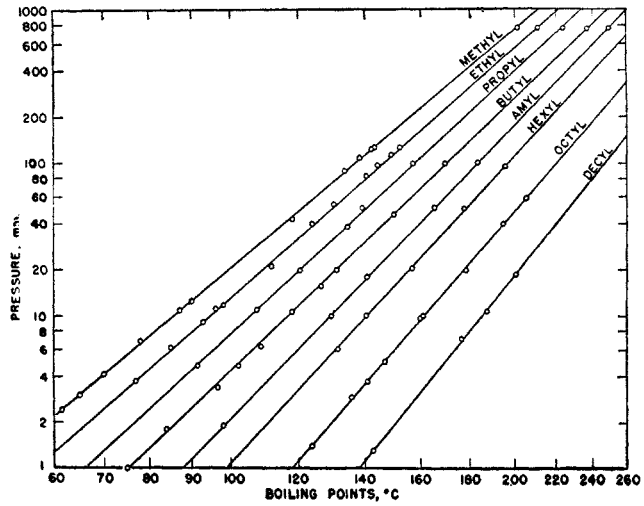

FIG. 1 BOILING POINTS OF n-ALKYL CARBONATES OF METHYL LACTATE

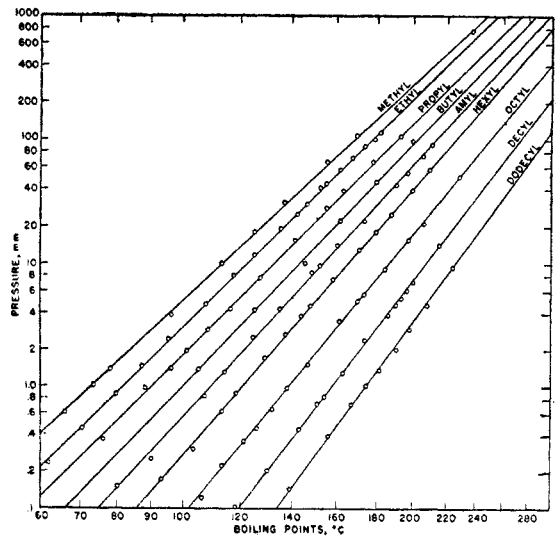

FIG. 2 BOILING POINTS OF n-ALKYL CARBONATES OF BUTYL LACTATE

atoms in the compounds. These lines, equations for which are shown in Table II, had a common point of intersection for each family. For the carbonates of methyl lactate, this point was where Log P = 6.78 and x = −13.6; for the butyl lactate derivatives, it was where Log P = 6.3 and x = −12. Also, within each family, the slopes (a) of these lines varied with the temperature:

TABLE II

EQUATIONS RELATING VAPOR PRESSURE (P) AT VARIOUS TEMPERATURES TO THE NUMBER OF CARBON ATOMS (x) IN *n*-ALKYL CARBONATES OF METHYL AND BUTYL LACTATES

$\log P = a x + b$

TEMP., °C.	a	b	DEVIATIONS,[a] %	
			Max.	Average
CARBONATES OF METHYL LACTATE				
100	−0.274	3.055	11	4
150	− .225	3.680	10	3
200	− .192	4.160	11	4
250	− .166	4.550	4	2
CARBONATES OF BUTYL LACTATE				
100	−0.270	3.240	10	5
150	− .214	3.697	7	3
200	− .181	4.145	4	2
250	− .154	4.480	5	2

[a] Deviations from the pressures read from Figures 1 and 2; methyl carbonates are excluded. A deviation of 5% corresponds to a difference in boiling point of about 1°.

TABLE III

EQUATIONS RELATING BOILING POINTS (T = °K) AT VARIOUS PRESSURES TO THE NUMBER OF CARBON ATOMS (x) IN *n*-ALKYL CARBONATES OF METHYL AND BUTYL LACTATES

$10^{-4} T^2 = a x + b$

PRESSURE, MM.	a	b	DEVIATIONS[a]	
			Max.	Average
CARBONATES OF METHYL LACTATE				
760	1.51	12.35	4	2.0
100	1.18	9.10	2	1.0
10	0.93	6.87	2	1.1
1	.78	5.23	2	.8
CARBONATES OF BUTYL LACTATE				
760	1.54	11.33	3	1.6
100	1.18	8.42	2	.7
10	0.93	6.20	2	.8
1	.75	4.95	2	1.1
0.1	.627	4.02	1	.4

[a] Deviations from boiling points read from Figures 1 and 2; methyl carbonates excluded.

For the methyl lactate series: $a = 0.048 - \frac{94}{t + 193}$

For the butyl lactate series: $a = 0.053 - \frac{92}{t + 193}$

By use of these equations for the slopes, and the common points given above, equations similar to those in Table II are readily calculated for any desired temperature.

TABLE IV

RELATIONSHIP OF REFRACTIVE INDEX AND DENSITY TO NUMBER OF CARBON ATOMS (x) IN *n*-ALKYL CARBONATES OF METHYL AND BUTYL LACTATES

EQUATIONS	DEVIATIONS[a] × 10^4	
	Max.	Average
CARBONATES OF METHYL LACTATE		
$\frac{x+5}{n_D^{20}} = 0.68x + 3.742$	5	2.4
$\frac{x+5}{n_D^{40}} = 0.6826x + 3.7755$	6	2.4
$\frac{x+3}{d_4^{20}} = 1.167x + 0.819$	27[b]	11
$\frac{x+3}{d_4^{40}} = 1.184x + 0.880$	22[b]	8
CARBONATES OF BUTYL LACTATE		
$\frac{x+6}{n_D^{20}} = 0.678x + 4.504$	6	2.4
$\frac{x+6}{n_D^{40}} = 0.681x + 4.537$	6	2.5
$\frac{x+2}{d_4^{20}} = 1.167x - 0.069$	19[c]	8[c]
$\frac{x+2}{d_4^{40}} = 1.183x$	14[c]	6[c]

[a] Difference between calculated and observed values of refractive index or density. Methyl carbonates excluded. [b] Maximum deviation was shown by the hexyl carbonate. [c] Octyl carbonate excluded; its deviation was 122 and 123 at 20° and 40°, respectively.

Table III consists of a set of equations relating boiling points, at certain fixed pressures, to the number of carbon atoms in the esters. Within each family, these lines pass through a common point as follows:

For the methyl lactate series: $10^{-4}T^2 = -2.3$, $x = -9.7$

For the butyl lactate series: $10^{-4}T^2 = -1.0$, $x = -8.0$

The slopes (a) of the lines are related to the pressure by the following equations:

For the methyl lactate series: $\text{Log } P = -4.61/a + 5.93$

For the butyl lactate series: $\text{Log } P = -4.11/a + 5.50$

These equations for the slope, together with the common points given above,

enable one to derive equations, similar to those in Table III, for boiling points at any desired pressure.

Densities and refractive indices. These constants were determined at 20° and 40°, and are recorded in Table I. Table IV shows empirical equations relating these constants to the number of carbon atoms in the compounds.

The last two equations in Table IV, which relate the densities of the carbonates of butyl lactate to the number of carbon atoms in the esters, yield calculated densities which show only small and random deviations from the observed values, with the exception of the octyl ester. The deviations of the calculated densities of this ester are 15 to 20 times the average deviations of the other esters; hence no weight was given this ester in the derivation of the equations. The reason for this large aberration is unknown. The ester was prepared twice, different lots of reagents being used. Each product was fractionally distilled until all determined

TABLE V

RELATION OF VISCOSITY (η = CPS.) TO NUMBER OF CARBON ATOMS IN *n*-ALKYL CARBONATES OF METHYL AND BUTYL LACTATES

$\text{Log } \eta_t = a\,x + b$

t, °C.	a	b	DEVIATIONS, CPS.[a]	
			Max.	Average
CARBONATES OF METHYL LACTATE				
20	0.062	0.242	0.80	0.25
40	0.054	0.036	0.34	0.20
CARBONATES OF BUTYL LACTATE				
20	0.055	0.176	0.60	0.31
40	0.049	−0.023	0.23	0.12

[a] Methyl carbonates excluded.

physical properties were constant. The two products had virtually identical properties and analyses. The boiling points, refractive indices, and viscosities had about the expected values; only the densities showed large deviations. The hexyl carbonate of methyl lactate showed a similar but smaller aberration.

Viscosities. Viscosities were determined at 20° and 40° (Table I). When plotted logarithmically *versus* the number of carbon atoms in the esters, straight lines were obtained, the equations of which are shown in Table V.

Solubilities. Table I shows the solubilities of the esters in water at 25°, determined by the method of Fordyce and Meyer (4). When the two alkyl groups in the esters contained a total of more than seven carbon atoms, the solubility was less than 0.01% and was too small to measure. The solubility of the carbonates of methyl lactate followed the equation $\text{Log } S = 3.81 - 0.513x$. The solubilities of the butyl lactate derivatives, when large enough to measure, were approximately equal to those of the isomeric methyl lactate carbonates.

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EXPERIMENTAL

Materials. The chloroformates up to the hexyl ester are commercially available. The higher ones were supplied by the U. S. Industrial Chemical Company. All were used as received.

Commercial methyl and butyl lactates were used after a fractional distillation. The higher lactates were prepared by the alcoholysis of methyl lactate (5). The lactates were treated with the chloroformates in the presence of pyridine as described in the first paper of this series (1).

Physical constants. Boiling points used in the construction of Figures 1 and 2 were determined by use of an improved tensimeter-still (6).

Refractive indices were measured with an Abbé type refractometer. Densities were determined with a Sprengel type pycnometer holding about 10 cc. Viscosities were measured with modified Ostwald pipettes calibrated with standard oils furnished by the Bureau of Standards. The constant temperature bath used for all these measurements was set to $\pm 0.1°$ and controlled to $\pm 0.02°$ (7).

SUMMARY

Three homologous series of esters, comprising twenty compounds, were prepared: (a) *n*-alkyl carbonates of methyl lactate, (b) *n*-alkyl carbonates of butyl lactate, and (c) butyl carbonates of *n*-alkyl lactates. The two latter series differ only in that their alkyl groups are interchanged, and their isomeric members have almost identical physical properties.

Equations were developed which relate vapor pressures, boiling points, refractive indices, densities, viscosities, and solubilities to the number of carbon atoms in the members of each series of esters.

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