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

C. E. REHBERG AND MARION B. DIXON

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Previous papers in this series described a group of miscellaneous carbonates of lactates (1) and three homologous families (2), and also indicated the usefulness of some of these esters as plasticizers for vinyl chloride resins (3). This paper describes two additional series of esters having the formula ROCOOCH (CH_3)COOR′. In one homologous series, R is ethyl and R′ is *n*-alkyl. In the other, R and R′ are identical *n*-alkyl groups. Each series consists of six members, one compound being common to both (Table I).

The esters were prepared, and physical properties were determined as described in a previous paper (2). The preparation and physical properties of the lactates used have been described recently (4).

Although the lowest members of each series have been prepared (2), they are not included in this paper because, as is usual in homologous series, their physical properties deviate from the orderly sequence shown by the higher members of the series.

Boiling points and vapor pressures. Figures 1 and 2 show the boiling points of the esters as a function of the pressure. In these modified Cox charts, pressure is plotted logarithmically, and the temperature scale is laid off as a linear function of $1/(t+193)$, where t is in °C. The lines showed considerable curvature (convex upward) when plotted on the usual types of Cox paper having temperature scales determined by $1/(t+273)$ or $1/(t+230)$, although the curvature was less with the latter type paper. The scales determined by $1/(t+193)$ were straight lines, and charts having this scale were conveniently prepared from commercial Cox chart paper having a scale linear with $1/(t+273)$ by adding 80° to each temperature designated on the chart. The mathematical proof of this transformation has been published elsewhere (5).

In each homologous series, the logarithm of the vapor pressure at any fixed temperature is a linear function of the number of carbon atoms in the ester. Tables II and III show equations for these lines at various temperatures. For each series, these lines constitute a family having a common point of intersection located as follows:

For the ethyl carbonate series: $x = -18$, $\log P = 7.5$.
For the alkyl carbonate series: $x = -14.5$, $\log P = 6.5$.

Also, within each family, the slopes (a) of these lines vary with the absolute temperature:

For the ethyl carbonate series: $a = -113/T + 0.055$.
For the alkyl carbonate series: $a = -130/T + 0.103$.

[1] One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

TABLE I

n-ALKYL CARBONATES OF *n*-ALKYL LACTATES: $ROCOOCH(CH_3)COOR'$

R	R'	YIELD, %	n_D^{20}	n_D^{40}	d_4^{20}	d_4^{40}	MOL. REFR. 20°		VISCOSITY, CPS.		C, %		H, %	
							Calc'd	Found	20°	40°	Calc'd	Found	Calc'd	Found
Ethyl	Ethyl	72	1.4112	1.4032	1.0742	1.0523	44.10	43.98	4.11	2.45	50.5	50.5	7.4	7.5
Ethyl	Butyl[a]	54	1.4181	1.4102	1.0325	1.0138	53.33	53.28	5.16	2.95	55.0	54.8	8.3	8.3
Ethyl	Hexyl	80	1.4242	1.4167	1.0021	0.9828	62.57	62.75	7.46	3.79	58.5	58.5	9.0	8.9
Ethyl	Octyl[b]	49	1.4281	1.4212	0.9846	0.9664	71.80	71.70	8.96	4.61	61.3	61.3	9.6	9.6
Ethyl	Dodecyl	48	1.4366	1.4295	0.9569	0.9406	90.27	90.41	15.64	7.51	65.4	65.4	10.4	10.5
Ethyl	Hexadecyl	90	1.4422	1.4352	0.9390	0.9235	108.75	108.97	25.48	11.57	68.4	68.6	10.9	10.9
Propyl	Propyl	70	1.4189	1.4110	1.0338	1.0136	53.33	53.31	5.88	3.20	55.0	55.0	8.3	8.2
Butyl	Butyl[a]	73	1.4240	1.4162	1.0049	0.9864	62.57	62.75	6.51	3.64	58.5	59.1	9.0	9.2
Amyl	Amyl[c]	67	1.4290	1.4214	0.9848	0.9670	71.80	71.82	8.74	4.57	61.3	61.3	9.6	9.4
Hexyl	Hexyl[c]	64	1.4327	1.4250	0.9654	0.9483	81.04	81.34	11.59	5.65	63.5	63.4	10.0	10.1
Decyl	Decyl[c]	25	1.4440	1.4358	0.9315	0.9157	117.98	118.22	25.66	11.68	69.5	69.8	11.2	11.1

[a] These compounds have been described previously (2), but are included here for comparison with their homologs. [b] Some of the data on this compound have been published previously (1). [c] Certain data on these compounds have been reported previously (3).

By use of these equations for the slopes, and the common points given above, equations for vapor pressures at any desired temperature may be readily calculated.

FIG. 1 BOILING POINTS OF ETHYL CARBONATES OF n-ALKYL LACTATES

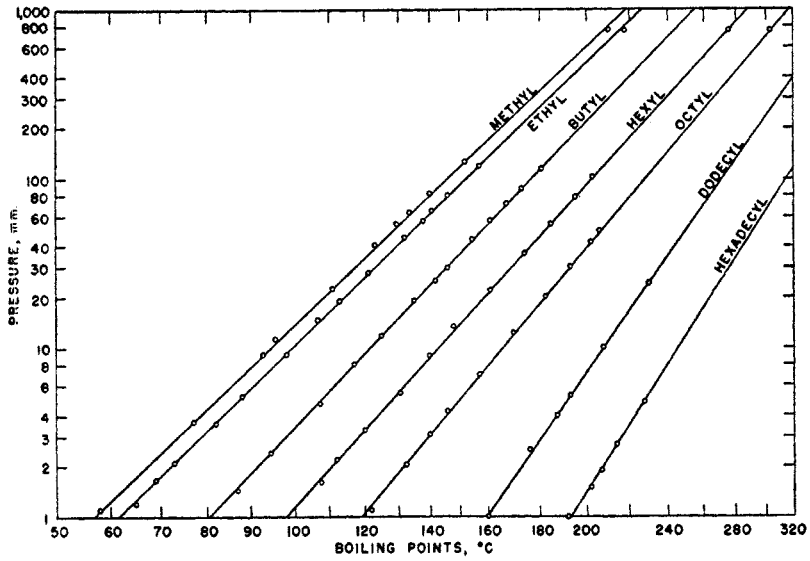
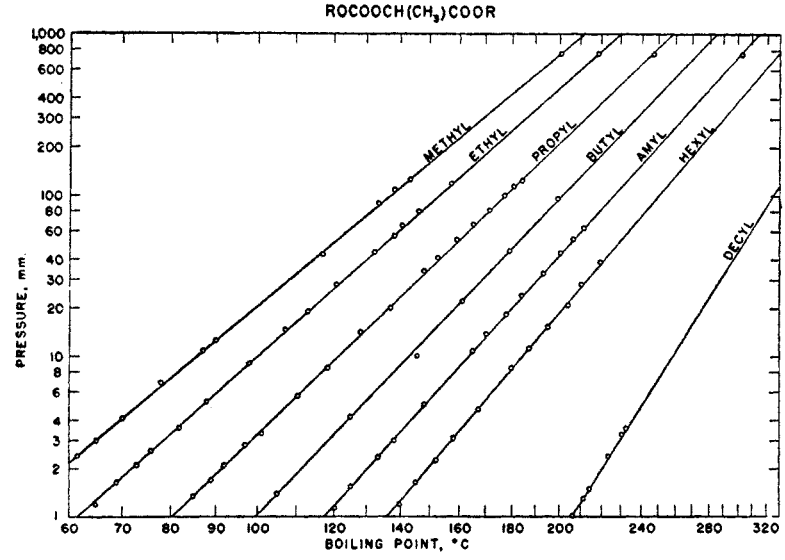


FIG. 2 BOILING POINTS OF n-ALKYL CARBONATES OF n-ALKYL LACTATES: ROCOOCH(CH_3)COOR



At any chosen fixed pressure, the squares of the boiling points (°K) vary directly with the number of carbon atoms in the esters of either series. Equations in Tables II and III show these relationships. Within each family, these lines determined at different pressures pass through a common point.

TABLE II

BOILING POINTS (T = °K.) AND VAPOR PRESSURES (P = PRESSURE, MM.) OF ETHYL CARBONATES OF *n*-ALKYL LACTATES AS RELATED TO NUMBER OF CARBON ATOMS (x)

CONST. TEMP., °C., OR PRESSURE, MM.	a	b	DEVIATIONS[a]	
			Max.	Average
Boiling Points: $10^{-4}T^2 = ax + b$				
760 mm.	1.56	11.30	3	1.2
100	1.18	8.50	1	0.7
10	0.918	6.50	3	1.8
1	0.746	5.18	4	2.0
Vapor Pressures: Log P = $ax + b$				
300°	−0.143	4.92	19	14
250	−0.161	4.57	9	7
200	−0.184	4.17	6	2
150	−0.212	3.67	2	1
100	−0.248	3.00	6	4

[a] Temperature deviations are in °C. Pressure deviations are in percentages. A deviation of 1° is equivalent to a pressure deviation of about 5%.

TABLE III

BOILING POINTS (T = °K.) AND VAPOR PRESSURES (P = PRESSURE, MM.) OF COMPOUNDS ROCOOCH(CH_3)COOR (R = *n*-ALKYL) AS RELATED TO NUMBER OF CARBON ATOMS (x)

CONSTANT TEMP., °C. OR PRESSURE, MM.	a	b	DEVIATIONS[a]	
			Max.	Average
Boiling Points: $10^{-4}T^2 = ax + b$				
760 mm.	1.51	11.95	2	0.6
100	1.15	8.80	5	1.7
10	0.896	6.60	2	1.0
1	0.734	5.12	2	1.3
Vapor Pressures: Log P = $ax + b$				
300°	−0.127	4.66	11	7
250	−0.145	4.35	7	4
200	−0.171	4.02	3	2
150	−0.202	3.57	4	2
100	−0.245	2.95	4	3

[a] Temperature deviations are in °C. Pressure deviations are in percentages. A deviation of 1° is equivalent to a pressure deviation of about 5%.

For ethyl carbonates: $x = -7.5$, $10^{-4}T^2 = -0.4$.
For alkyl carbonates: $x = -9.0$, $10^{-4}T^2 = -1.5$.

The slopes (a) of these lines vary inversely with the logarithm of the pressure (P):

For the ethyl carbonates: $\text{Log P} = -4.21/a + 5.59$.

For the alkyl carbonates: $\text{Log P} = -4.21/a + 5.69$.

By use of these equations for the slopes and the common points given above, equations may be calculated for boiling points at any desired pressure.

Densities, refractive indices, and viscosities. These physical properties were measured at 20° and at 40° (Table I). As reported in the previous paper (2), linear relationships were found between certain functions of these physical constants and the number of carbon atoms in the esters. Table IV shows equations for these relationships. These equations are highly useful, not only for calculating the properties of homologs not prepared but for checking the purity

TABLE IV

EQUATIONS RELATING REFRACTIVE INDICES, DENSITIES, AND VISCOSITIES TO THE NUMBER OF CARBON ATOMS IN CARBONATES OF LACTATES ROCOOCH(CH$_3$)COOR′

R	R′	EQUATION	DEVIATIONS[a]	
			Max.	Average
Ethyl	*n*-Alkyl	$1/(x + 10) = -0.773\ n_D^{20} + 1.1462$	0.0007	0.0002
Ethyl	*n*-Alkyl	$1/(x + 10) = -0.741\ n_D^{40} + 1.095$	0.0005	0.0002
Ethyl	*n*-Alkyl	$1/x = 0.583\ d_4^{20} - 0.5019$	0.0017	0.0008
Ethyl	*n*-Alkyl	$1/x = 0.618\ d_4^{40} - 0.5253$	0.0020	0.0009
Ethyl	*n*-Alkyl	$\text{Log } \eta_{20} = 0.0566\ x + 0.161$	6.7[b]	2.3[b]
Ethyl	*n*-Alkyl	$\text{Log } \eta_{40} = 0.0495\ x - 0.030$	3.3[b]	1.6[b]
R = R′ =	*n*-Alkyl	$1/(x + 8) = -0.954\ n_D^{20} + 1.4088$	0.0005	0.0002
	n-Alkyl	$1/(x + 8) = -0.954\ n_D^{40} + 1.4012$	0.0005	0.0002
	n-Alkyl	$1/(x + 1) = 0.498\ d_4^{20} - 0.4238$	0.0005[c]	0.0002[c]
	n-Alkyl	$1/(x + 1) = 0.521\ d_4^{40} - 0.4371$	0.0002[c]	0.0002[c]
	n-Alkyl	$\text{Log } \eta_{20} = 0.0500\ x + 0.240$	7.3[b]	5.4[b]
	n-Alkyl	$\text{Log } \eta_{40} = 0.0424\ x + 0.065$	3.8[b]	2.6[b]

[a] Difference between calculated and observed values of the physical constants; methyl esters excluded. [b] Percentage deviation from the observed value. [c] Hexyl carbonate of hexyl lactate excluded; its deviation was .0037 at 20° and .0035 at 40°.

of those studied and the accuracy of physical measurements made on them. When such correlations of physical properties with molecular structure have been made for a sufficient number of families of compounds, broader and more fundamental relationships may become demonstrable.

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SUMMARY

Two homologous series of *n*-alkyl carbonates of *n*-alkyl lactates, ROCOOCH(CH$_3$)COOR′, were prepared, and several physical properties were determined. In one series R is ethyl and R′ is *n*-alkyl; in the other R and R′ are identical *n*-alkyl groups.

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

PHILADELPHIA 18, PA.

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