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MIXED ESTERS OF LACTIC AND CARBONIC ACIDS. *n*-ALKYL CARBONATES OF VARIOUS LACTATES[2]

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Previous papers (1–3) have described five homologous series of carbonates of *n*-alkyl lactates, in addition to several miscellaneous esters. Three additional homologous series—the *n*-alkyl carbonates of tetrahydrofurfuryl lactate, 2-butoxyethyl lactate and 2-(2-butoxyethoxy)ethyl lactate—are described in this paper. Data on the use of most of these esters as plasticizers have been presented (4), but will be published elsewhere.

The esters, shown in Table I, were made by treating the lactate with an alkyl chloroformate in the presence of pyridine (1). As in the previous studies, boiling points, refractive indices, densities, and viscosities of the products were determined (Table I), and these physical properties were correlated with the number of carbon atoms in the members of each homologous series.

Boiling points and vapor pressures. Figures 1–3 show the boiling points of the esters as a function of the pressure. As in the previous papers, the temperature scale of Figures 1–3 are laid off as linear functions of $1/(t + 193)$, where t is the temperature in °C.

For each series, straight lines were obtained by plotting the logarithm of the vapor pressure at any fixed temperature *versus* the number of carbon atoms (x) in the compounds. These lines, equations for which are shown in Table II, had a common point of intersection for each family as follows: tetrahydrofurfuryl series, $\log P = 5.8$, $x = -14$; butoxyethyl series, $\log P = 5.3$, $x = -9.3$, and butoxyethoxyethyl series, $\log P = 9.0$, $x = -32$. Also, the slope (a) of these lines for each series was found to be a linear function of the absolute temperature: for the tetrahydrofurfuryl series, $a = 0.156 - 152/T$; for the butoxyethyl series, $a = 0.275 - 165/T$; and for the butoxyethoxyethyl series, $a = 0.027 - 92.8/T$ By use of these equations for the slope, and the common points of intersection given above, equations similar to those in Table II may be calculated for the vapor pressures of the members of either of the three series of esters at any temperature.

At any fixed pressure, the squares of the boiling points (°K) varied linearly with the number of carbon atoms in the esters of each series. Coefficients for the equations for these lines are shown in Table III. For each series, the lines defined by the equations of Table III had a common point of intersection having the following coordinates: For the tetrahydrofurfuryl esters: $10^{-4}T^2 = -1.8$,

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[2] Many of the compounds reported in this paper have been tested to determine their utility as plasticizers, and the results were included in a paper presented before the Division of Paint, Varnish and Plastics Chemistry at the Washington Meeting of the American Chemical Society, August-September, 1948.

TABLE I

ALKYL CARBONATES OF LACTIC ESTERS

REACTANTS		YIELD, %	n_D^{20}	n_D^{40}	d_4^{20}	d_4^{40}	MOL. REFRACTION		VISCOSITY, CPS.		C		H	
Chloroformate	Lactate						Calc'd	Found, 20°	At 20°	At 40°	Calc'd.	Found	Calcd.	Found
Ethyl	Tetrahydrofurfuryl	73	1.4430	1.4358	1.1384	1.1195	57.39	57.36	22.86	10.37	53.6	53.2	7.4	7.3
n-Butyl	Tetrahydrofurfuryl	59	1.4451	1.4381	1.0958	1.0785	66.63	66.64	28.41	12.23	56.9	56.6	8.1	8.1
n-Hexyl	Tetrahydrofurfuryl	50	1.4470	1.4400	1.0632	1.0479	75.86	76.00	30.98	13.81	59.6	59.4	8.7	8.7
n-Octyl	Tetrahydrofurfuryl	43	1.4486	1.4416	1.0370	1.0221	85.10	85.39	34.98	14.40	61.8	61.8	9.1	8.9
n-Decyl	Tetrahydrofurfuryl	66	1.4500	1.4430	1.0166	1.0020	94.34	94.75	39.99	16.13	63.7	63.7	9.6	9.7
n-Dodecyl	Tetrahydrofurfuryl	57	1.4510	1.4438	0.9990	0.9861	103.57	104.17	45.63	18.52	65.3	65.8	9.9	10.2
Ethyl	2-(2-Butoxyethoxy)ethyl	—	1.4330	1.4252	1.0507	1.0322	75.09	75.78	14.44	6.95	54.9	55.3	8.6	8.6
n-Amyl	2-(2-Butoxyethoxy)ethyl	74	1.4366	1.4296	1.0247	1.0070	88.94	89.02	18.69	8.70	58.6	58.6	9.3	9.3
n-Octyl	2-(2-Butoxyethoxy)ethyl	56	1.4402	1.4330	0.9984	0.9823	102.80	103.14	22.39	10.22	61.5	61.4	9.8	9.8
n-Decyl	2-(2-Butoxyethoxy)ethyl	31	1.4422	1.4350	.9864	.9698	112.04	112.32	26.51	11.86	63.1	63.2	10.1	10.1
n-Dodecyl	2-(2-Butoxyethoxy)ethyl	52	1.4444	1.4372	.9734	.9571	121.27	121.95	32.64	14.44	64.6	65.0	10.4	10.7
Ethyl	2-Butoxyethyl	69	1.4268	1.4195	1.0481	1.0292	64.21	64.24	9.70		54.6	54.9	8.5	8.5
n-Amyl	2-Butoxyethyl	54	1.4314	1.4242	1.0112	0.9930	78.06	78.07	12.98	6.33	59.2	59.3	9.3	9.4
n-Decyl	2-Butoxyethyl	62	1.4392	1.4320	0.9640	.9479	101.15	101.21	19.30	9.14	64.1	64.6	10.2	10.5
n-Hexyl	2-Phenoxyethyl	69	1.4812	1.4740	1.0861	1.0685	88.31	88.70	84.68	25.13	63.9	63.7	7.7	7.6
n-Hexyl	2-*n*-Hexyloxyethyl	78	1.4367	1.4286	0.9841	0.9670	91.92	92.17	17.05	8.02	62.4	62.4	9.9	9.8
n-Hexyl	Diethylene glycol	61	1.4454	1.4380	1.0847	1.0678	124.58	124.41	150.9	44.47	56.9	56.6	8.4	8.4
Ethyl	Diethylene glycol	70	1.4396	1.4324	1.1844	1.1654	87.63	87.67	321.0	60.25	48.7	48.4	6.7	6.8
Methyl	*n*-Decyl	59	1.4330	1.4258	0.9793	0.9622	76.42	76.53	12.71	6.16	62.5	62.5	9.8	9.7

$x = -14.5$; for the butoxyethyl esters: $10^{-4}T^2 = -2.0$, $x = -9.0$; for the butoxyethoxyethyl esters: $10^{-4}T^2 = 3.5$, $x = -5.0$. Also, the slopes (a) of these lines varied linearly with the logarithm of the pressure: for tetrahydrofurfuryl esters: $\log P = 5.75 - 3.91/a$; for butoxyethyl esters: $\log P = 5.34 - 4.35/a$; for butoxyethoxyethyl esters: $\log P = 4.00 - 2.80/a$. By use of these slopes and

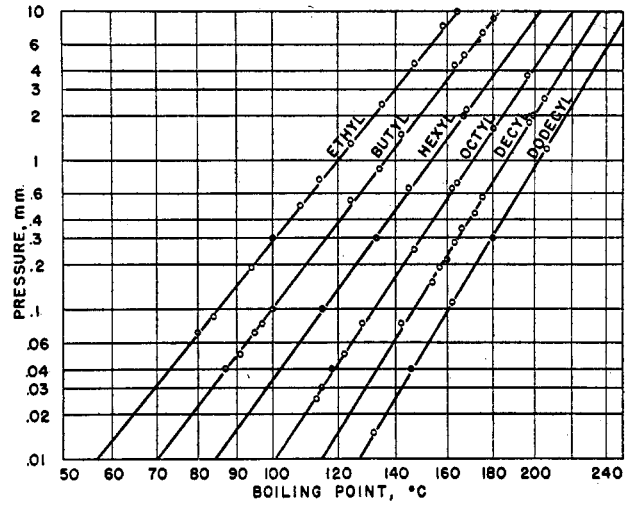

FIG. 1. BOILING POINTS OF n-ALKYL CARBONATES OF TETRAHYDROFURFURYL LACTATE

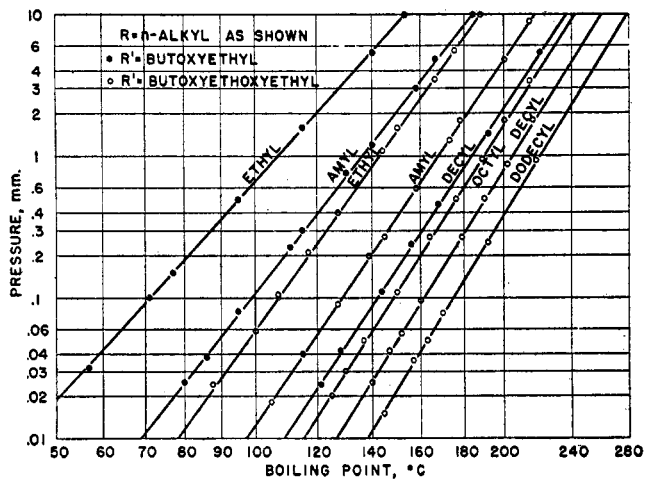

FIG. 2. BOILING POINTS OF CARBONATES, ROOCOCH(CH_3)COOR′

the common points given above, equations similar to those in Table III may be calculated for any pressure.

A more general, but less accurate, equation for the boiling points of carbonates of lactates ROCOOCH(CH_3)COOR′ is

$$A = 0.49\ (B + C) - 14$$

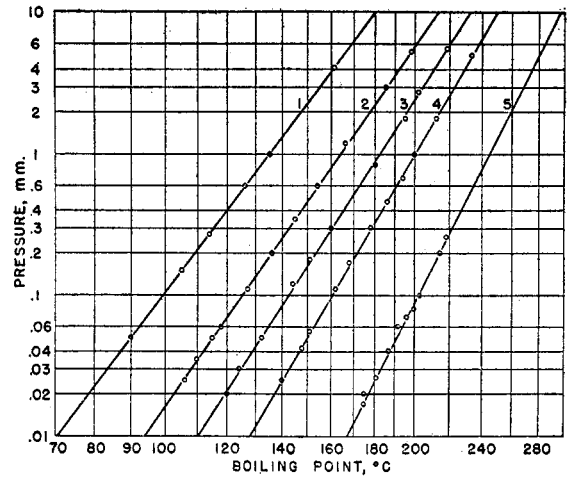

FIG. 3. BOILING POINTS OF MISCELLANEOUS CARBONATES: 1. Methyl carbonate of decyl lactate. 2. *n*-Hexyl carbonate of 2-*n*-hexyloxyethyl lactate. 3. *n*-Hexyl carbonate of 2-phenoxyethyl lactate. 4. Ethyl carbonate of diethylene glycol dilactate. 5. *n*-Hexyl carbonate of diethylene glycol dilactate.

TABLE II

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

LOG P = $ax + b$

TEMP., °C.	*a*	*b*	DEVIATIONS[a], %	
			Max.	Av.
Carbonates of Tetrahydrofurfuryl Lactate				
100	−0.252	2.28	6	4
150	−.203	2.96	5	3
200	−.166	3.47	5	3
Carbonates of Butoxyethoxyethyl Lactate				
100	−.222	1.865	1	1
150	−.191	2.87	10	6
200	−.168	3.59	10	6
250	−.151	4.18	1	0.4
Carbonates of Butoxyethyl Lactate				
110	−.256	2.90	4	3
135	−.229	3.16	5	4
160	−.206	3.44	16	14

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

where A = boiling point of the ester at 1-mm. pressure, and B and C are the normal boiling points of the alcohols ROH and R′OH. This equation shows a

maximum deviation of 13° and an average deviation of 2.9° from the observed boiling points of 55 esters reported in this paper and the preceding papers of this series.

Densities and refractive indices. These physical properties were measured at 20 and 40° (Table I). As in the previous papers, linear relationships were found between certain functions of these physical constants and the number of carbon atoms in the esters in each series. These equations are shown in Table IV. Such equations are useful, not only for calculating the properties of homologs not

TABLE III

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

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

PRESSURE, MM.	a	b	DEVIATIONS, °K.	
			Max.	Av.
Carbonates of Tetrahydrofurfuryl Lactate				
0.01	0.502	5.36	2	1.2
.10	.580	6.50	2	1.2
1.00	.686	8.00	2	1.0
10.0	.826	10.17	2	1.0
Carbonates of Butoxyethyl Lactate				
0.01	0.593	3.33	0	0
.10	.687	4.17	2	0.5
1.00	.816	5.34	2	.7
10.0	.996	7.00	3	1.0
Carbonates of Butoxyethoxyethyl Lactate				
0.01	0.462	5.81	1	0.3
.10	.572	6.35	1	.8
1.00	.714	7.15	2	.9
10.0	.923	8.12	3	1.5

prepared but for checking the purity of those studied and the accuracy of the physical measurements made on them.

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EXPERIMENTAL

Lactates. The preparation of tetrahydrofurfuryl, 2-butoxyethyl, 2-(2-butoxyethoxy)-ethyl, and n-decyl lactates has been described (5–7).

2-Hexyloxyethyl and 2-phenoxyethyl lactates were prepared from methyl lactate by the alcoholysis procedure (7).

In attempts to prepare diethylene glycol dilactate by the reaction of equivalent amounts of diethylene glycol and methyl lactate, 30 to 40% yields of lactide were obtained. An equal

amount of monolactate was produced, but the yield of dilactate was much lower. A small fraction, thought to be a trilactate, was obtained (Table V). Despite many experiments, no satisfactory procedure was found for the preparation of a glycol dilactate.

The lactates not previously reported in the literature are shown in Table V.

TABLE IV

EQUATIONS FOR THE DENSITY AND REFRACTIVE INDEX OF CARBONATES OF LACTATES

EQUATION	DEVIATIONS	
	Max.	Av.
Carbonates of Tetrahydrofurfuryl Lactate		
$1/(x + 10) = -1.857\ n_D^{20} + 2.7272$	0.0002	0.0001
$1/(x + 10) = -1.700\ n_D^{40} + 2.4876$	.0005	.0002
$1/(x + 2) = 0.240\ d_4^{20} - .1963$	.0004	.0002
$1/(x + 2) = .251\ d_4^{40} - .2040$	.0008	.0003
Carbonates of Butoxyethyl Lactate		
$1/(x + 25) = -0.3889\ n_D^{20} + 0.5818$	.0003	.0003
$1/(x + 25) = -.3887\ n_D^{40} + .5787$	.0004	.0003
$1/(x + 12) = .1242\ d_4^{20} - .0885$	.0004	.0002
$1/(x + 12) = .1282\ d_4^{40} - .09027$	.0001	.0000
Carbonates of Butoxyethoxyethyl Lactate		
$1/(x + 25) = -0.458\ n_D^{20} + 0.6819$	.0003	.0002
$1/(x + 25) = -.440\ n_D^{40} + .6527$	.0003	.0001
$1/(x + 10) = .156\ d_4^{20} - .1225$	.0023	.0009
$1/(x + 10) = .162\ d_4^{40} - .1258$	.0021	.0010

TABLE V

PREPARATION OF LACTATES

LACTATE	YIELD, %	B.P., °C.	PRESS., MM.	n_D^{20}	d_4^{20}	MOL. REFRACT.		SAPON. EQUIV.		C		H	
						Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
2-Hexyloxyethyl	83	86	1	1.4362	0.9829	57.82	58.09	218.3	223.3	60.5	60.9	10.2	10.5
2-Phenoxyethyl	30	102	0.2	1.5102	1.1613	54.22	54.16	210.2	199	62.8	62.4	6.7	6.9
Diethylene glycol monolactate	39	96	.1	1.4560	1.1819	40.87	40.98	178.2	177.6	47.2	47.5	7.9	8.0
dilactate	14	120	.1	1.4582	1.2088	56.38	56.52	125.1	121.7	48.0	48.0	7.2	7.2
trilactate	3	145	.1	1.4588	1.2160	71.89	72.44	107.4	110.8	48.4	49.0	6.9	7.1

Preparation of carbonates and determination of physical constants. The lactates were treated with the alkyl chloroformates (used as received) in the presence of equivalent amounts of pyridine, as described in the earlier papers of this series. Similarly, the previously described procedures were used for the determination and correlation of physical constants.

SUMMARY

Nineteen alkyl carbonates of lactic esters, comprising three homologous series, were prepared. In each series, the vapor pressures, boiling points, refractive indices, densities and viscosities were correlated with the number of carbon atoms in the compounds.

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