

# of Lactic Acid and Derivatives



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# The Physical Properties of Lactic Acid and Derivatives

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A literature review

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# SUMMARY.

Lactic acid is an important chemical, used in food-technology, medicine and cosmetics. It's 2-hydroxypropionic acid.

This paper deals with the physical properties of lactic acid and it's derivatives.

There's not much known about the physical properties of pure lactic acid, because lactic acid appears mainly in the form of aqueous solutions. When physical properties of these solutions have been estimated one should consider that lactic acid in solution undergoes intermolecular esterification spontaneously, resulting after some time in an equilibrium solution containing, lactic acid, lactoyllactic acid, polylactic acid and a very little dilactide.

When it's not mentioned whether intermolecular esters are present in lactic acid solutions, physical properties of these solutions are not that reliable.

Also physical properties of lactic with other solvents than water are considered, like distribution coefficients, ternary phase diagrams and critical solution temperatures.

The optical activity of lactic acid doesn't have any influence on the physical properties, except the melting point. Racemic lactic acid has a lower melting point than optical active lactic acid, 25-27 °C and 52.7-52.8 °C respectively.

Also the physical properties of the intermolecular esters and some derivatives, are described. Not much is known about these esters. More is known about some common esters of lactic acid, like alkyl lactates.

The physical properties of alkali and ammonium lactates, salts of lactic acid, are mentioned shortly.

Some short articles deal with spectra of lactic acid. Here ultraviolet, infrared and microwave spectra are briefly discussed.

Most of the data presented were published more than 40 years ago, one article was even published in 1894. Unfortunately there aren't any recent articles about physical properties of lactic acid and derivatives.

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LITERATURE APPENDIX

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#### 1 HISTORY.

Lactic acid was first discovered in 1780 by the Swedish chemist Scheele [1]; it is 2-hydroxy-propionic acid:

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The French chemists Thenard, Fourcroy and Vauquelin and Bouillon-Lagrange denied that Scheele's lactic acid was an individual compound and their conclusions were that the acid consisted of acetic acid combined with an animal material, which modified the properties of the acid, making it less volatile, and in addition some other impurities. These statements caused the Swedish chemist Berzelius to repeat Scheele's experiments, and he concluded that lactic acid was an individual compound.

Lactic acid was rediscovered in 1813 by the French chemist Braconnot. The properties of Braconnot's acid corresponded closely to those of Scheele's acid, but, with reference to Bouillon-Lagrande, Braconnot concluded that he had found a new individual acid.

Shortly thereafter the German chemist Vogel proved the identity of Scheele's and Braconnot's acid.

Originally the lactic acid of fermentation and that found in muscle tissue were regarded as identical. Liebig, who in 1847 re-examined meat extract, suspected that the two acids might not be identical. He asked Engelhardt to carry out an examination of the salts of the two acids. Engelhardt confirmed Liebig's impression that the contents of water of crystallization and the solubilities of the salts of the two lactic acids differed, and thus that the acids were different.

The solution of the problem was predicted by Wislicenus, who discovered the optical activity of lactic acid. The isomeric lactic acids were thus the first case in which with certainty more isomers were known than the number of possible structures, and Wislicenus proposed that the explanation should be found in the conception of different placings of the atoms in space. The principal source of lactic acid is the lactic acid fermentation. The formation of lactic acid in milk was early recognized as a kind of fermentation.

In 1839 Frémy performed lactic acid fermentation of several carbohydrates, such as cane sugar, milk sugar, mannite, starch, and dextrin, a discovery that was confirmed by Gay-Lussac, and in 1840 Louradour prepared lactic acid by fermentation of whey and converted it into iron(II) lactate by dissolution of metallic iron in it. Industrial manufacture of lactic acid was first established in 1881 in the U.S.A., and in 1895 in Germany.

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# 2 APPLICATIONS OF LACTIC ACID.

Lactic acid had been known for many years before it was possible to make it. After its identity and properties were known, and suitable micro-organisms were found which could make the desired form of the acid, procedures and principles for the plants were worked out. Since then lactic acid has gained increasing importance and a great variety of applications of the acid, its salts and esters, and many other derivatives, have been developed.

The applications of lactic acid can be divided into two principal classes:

- 1 applications in food, medicine and cosmetics.
- 2 application as a chemical in chemistry and technology.

#### 2.1 Applications in food, medicine and cosmetics.

One of the most inportant outlets for lactic acid is the food industry. The properties that make it particularly suitable for consumption in food products are:

- It has a mild acid taste.
- It does not mask or overpower weakly aromatic flavours
- It functions as a preservative, or as a regulator of the microflora.
- It is a liquid, which makes it easily applicable.
- It occurs naturally in many food ingredients and thus it does not introduce a foreign element into the food.
- Its salts are soluble and they can in many cases partly replace the acid.

The variety of favourable food-technological properties makes it an additive of great value. A very important fact is that lactic acid and its common salts are completely non-toxic.

As an acidulant, lactic acid is widely used in combination with other acids; for instance lactic acid will when added to vinegar yield a milder and more subtle acid taste.

Calcium lactate has found certain applications in connection with preserving fruit; it preserves the firmness of apple slices during processing, and it inhibits discoloration of fruit and some vegetables.

The selective influence on microflora is utilized in breweries, lactic acid is used here to adjust the pH of hard water and also elsewhere during the manufacture of beer.

An application by which lactic acid and some of its derevatives have gained increasing importance was found in the manufacture of bread.

Over the years lactic acid and its salts have been mentioned for various medical uses. Although for some indications better specific means were found, lactic acid and lactates are still of recognized value.

Some of the early applications of lactic acid were directed against certain epidemic and other

bacterial diseases and their side effects. Lactic acid was often applied locally and the regulating effect on the microflora was thus utilized.

An important medical application nowadays is the use of the polyester of lactic acid, of which thread for surgery or protheses are being made.

#### 2.2 Application as a chemical in chemistry and technology.

The chemical-technological applications of lactic acid cover a much greater range. As a whole, lactic acid and its derivatives have found applications or have been proposed in a wide variety of branches of technology.

Lactic acid and its derivatives are mentioned in connection with a variety of resins and other polymeric products, and the possible uses extend from polymerizable monomers and raw materials for their preparation to components in copolymers and to technical additives such as solvents and plasticizers. The polyester of lactic acid, shows promising properties; for example, as said before, in the medical world.

In the tanning industry lactic acid is useful for deliming hides and the quality of the resulting leather is good.

Other uses of lactic acid are found in lithographic developers and in various types of ink; in these cases it is, however, often applied in the form of salts.

A variety of uses of lactic acid in connection with tectiles have been found. Thus some lactates have been recommended as mordants for colouring and printing various textiles.

During the last decades lactic acid has gained a surprisingly prominent position both in food technology and in chemical technology. The possibilities for the application are far from exhausted in any of the fields mentioned. Especially polylactide becomes more and more important because it's biodegradable, and so it doesn't pollute the environment.

#### **<u>3 PHYSICAL PROPERTIES OF LACTIC ACID.</u>**

# 3.1 Introduction.

Lactic acid is, when pure and anhydrous, a white crystalline solid with a low melting point. Because of the physical properties and the difficulties in the preparation of the pure and anhydrous acid this material is rare. Lactic acid appears in the form of concentrated aqueous solutions, as syrupy liquids. Solutions of good quality are colourless and practically odourless.

Lactic acid in solution undergoes intermolecular esterification spontaneously, resulting in the formation of lactoyllactic acid, the mutual ester of two molecules of lactic acid; polylactic acid, the chain polyesters containing more lactic acid units in the molecule, and a little dilactide, the cyclic mutual ester of lactic acid (fig. 1). Most of the data of physical properties given refer to racemic acid, but many of these properties are not affected by the optical composition. An important exception is the melting point of crystalline lactic acid.

When crystalline lactic acid free of intermolecular esters has been obtained by carefull distillation, then formation of lactoyllactic acid immediately starts, and this results in release of water from the reaction.



There is not much information about the physical properties of pure and crystalline lactic acid. Because lactic acid appears mainly in the form of concentrated aqueous solutions, the next chapters give information of the physical properties of these solutions.

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Figure 1: PT-diagram of lactic acid.



# 3.2 Melting point of pure crystalline lactic acid.

Crystalline lactic acid can be optically active or racemic. The melting point for each of the optical isomers is 52.7-52.8°C [2]. The melting point for the racemic acid is 25-27°C. The best melting point of racemic acid is not as sharp as the melting points of the single optical isomers.

# 3.3 Boiling points of pure lactic acid.

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The difference between the boiling points of racemic and optically active lactic acid is small. The boiling points of anhydrous lactic acid has been reported by several authors [1]. The values given in table 1 are estimated by Purac Biochem (Gorinchem, The Netherlands).

Pressure (Pa)	Temperature (K)
280	373.95
500	378.15
750	382.15
1000	387.25
1500	393.75
2000	398.85
2500	403.15
3000	406.15
4000	411.55
5000	415.75
7500	423.15

TABLE 1: Observed boiling points of anhydrous lactic acid.

A PT-diagram of lactic acid is given in figure 2.

At atmospheric pressure lactic acid has a virtual boiling point of 205°C. At this temperature lactic acid polymerises very rapidly, so the boiling point of pure anhydrous can't be estimated.

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# 3.4 Optical activity

Most physical properties of optically active lactic acid do not differ from the racemic acid. Important exceptions are the melting points of the pure and crystalline compounds.

Lactic acid is one of the oldest known examples of compounds in which one asymmetric centre is present. This asymmetric carbon atom carries the four different groups: -COOH, -H, -OH, and CH<sub>3</sub>. Molecular models of the optical isomers are shown in fig. 3.



fig. 3: Models of L(+)Lactic acid and D(-)Lactic acid.

These kind of pictures are not practical and in general, the Fischer projection is used.





The assignments (+) and (-) introduced above refer only to the sign of the rotation; steric relationship and absolute configuration must be expressed in other ways. D and L are used to describe the configuration.

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L (+) Lactic acid D (-) Lactic acid

#### fig. 5: Absolute configuration of Lactic acid

L(+) Lactic acid is dextro-rotatory with specific rotation,  $[\alpha]_{546.1 \text{ nm}} (T=21-22^{\circ}\text{C}) = +2.6^{\circ}$ , and D(-) Lactic acid is levo-rotatory with specific rotation  $[\alpha]_{546.1 \text{ nm}} (T=21-22^{\circ}\text{C}) = -2.6^{\circ}$ . [3,4]

#### **4 PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS OF LACTIC ACID.**

#### 4.1 Introduction.

In the following sections the physical properties of aqueous solutions of lactic acid are given. The data cover the concentration range from 0% to 90% by weight, and in some cases also higher concentrations.

The ideal data of aqueous solutions of lactic acid should be those representing lactic acid free of intermolecular esters, but such solutions are not stable (see 3.1). Aqueous solutions free of intermolecular esters can be made by dissolving purified crystalline lactic acid in water, but a few hours later such solutions contain substantial amounts of latoyllactic acid.

The data presented are subjected to some uncertainty because it is not always known if the solutions contain lactoyllactic acid in equilibrium with lactic acid.

Most of the data refer to equilibrated solutions.

In table 2 data is presented about lactic acid in equilibrium with lactoyllactic acid.[5]

Total Lactic acid weight %	Free Lactic acid weight %	Lactoyllactic acid weight %	Lactoyllactic acid % of Total lactic acid
6.29	6.02	0.24	4.2
12.19	11.70	0.44	4.0
25.02	22.60	2.18	9.7
37.30	32.80	4.04	12.1
54.94	48.20	6.05	12.3
88.60	58.60	26.90	33.8

TABLE 2: Compositions of lactic acid solutions. Lactic acid in equilibrium with lactoyllactic acid.  $(T=21^{\circ}C)$ .

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Figure 6 : Density of lactic acid solutions as a function of concentration, at constant temperatures. A=20°C, B=25°C, C=50°C, D=80°C.



Figure 7: Density of lactic acid solutions as a function of temperature, at constant concentrations.

A=0% (lactic acid by weight), B=9.16%, C=24.35%, D=45.48%, E=64.89%, F=85.32%.

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#### 4.2 Density.

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Densities of aqueous solutions of lactic acid of various concentrations have been determined by Troupe, Aspy and Schrodt [6]. The results are recorded in Table 3 and illustrated in Fig. 6 and 7, from which it can be seen that the density varies almost linearily with concentration and temperature. These data were obtained with solutions of lactic acid in equilibrium with lactoyllactic acid (Table 2).

Lactic acid		Тетр.	(°C)		
weight %	20	25	50	70	80
0	0.99823	0.99707	0.98807	0.97781	0.97183
9.16	1.01955	1.01811	1.00674	0.99504	0.98899
24.35	1.05678	1.05446	1.04146	1.02958	1.02260
45.48	1.10980	1.10536	1.08703	1.07219	1. <b>06399</b>
64.89	1.15526	1.15181	1.13205	1.11532	1.10762
75.33	1.17860	1.17482	1.15262	1.13407	1.12511
85.32	1.19890	1.19480	1.17180	1.15310	1.14430

TABLE 3: Densities of aqueous solutions of lactic acid. Variation with concentration and temperature. Lactic acid in equilibrium with lactoyllactic acid. (Densities, g/ml.)

Each series of results from all the above mentioned measurements have been subjected to approximation by using the method of least squares. The calculations demonstrated primarily that the variation of density was sufficiently well described when an approximating polynomial of the third degree was applied.

The coefficients of the calculated polynomials are given in Table 4. The polynomials are of the form:

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Figure 8 : Viscosity of lactic acid solutions as a function of concentration, at constant temperatures. A=30°C, B=40°C, C=50°C, D=60°C, E=70°C, F=80°C.

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Figure 9: Viscosity of lactic acid solutions as a function of temperature, at constant concentrations.

A=9.16% (lactic acid by weight), B=24.35%, C=45.48%, D=64.89%, E=75.33%, F=85.32%.

**Density** =  $\mathbf{a}_0 + \mathbf{a}_1^* \mathbf{c} + \mathbf{a}_2^* \mathbf{c}^2 + \mathbf{a}_3^* \mathbf{c}^3$ , where c is the concentration of lactic acid in percent by weight.

Temperature (°C)	a <sub>o</sub>	<b>a</b> 1	$a_2^*10^6$	a <sub>3</sub> *10 <sup>8</sup>
20	0.99823	0.0022955	6.2708	-6.5856
25	0.99707	0.0022277	6.4819	-6.3340
30	0.99567	0.0021709	6.5109	-6.1320
40	0.99224	0.0020977	6.2961	-5.7418
50	0.98807	0.0020238	6.7442	-6.0979
60	0.98324	0.0019666	6.1128	-5.2650
70	0.97781	0.0018541	9.6773	-8.2377
80	0.97183	0.0019174	5.6451	-5.2037

TABLE 4: Coefficients	for	polynomials	for	calculation	of	densities	of	aqueous
solutions of lactic acid.								

# 4.3 Viscosity.

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The viscosities of aqueous solutions of lactic acid were also determined by Troupe, Aspy and Schrodt [6] and by Vidler [5]. The solutions used for the determination of densities of solutions of lactic acid were again used here. It was shown that the viscosity increased rapidly with the concentration and decreased rapidly with increasing temperature. The measured values are given in table 5, and the variation of the viscosity with concentration and temperature is illustrated in Fig. 8 and 9.

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Lactic acid	Temp. (°C)					
weight %	30	40	50	60	70	80
0	0.8007	0.656	0.5494	0.4688	0.4061	0.3165
9.16	1.03	0.809	0.671	0.571	0.473	0.416
24.35	1.46	1.13	0.918	0.746	0.632	0.532
45.48	2.74	2.03	1.59	1.26	1.02	0.843
64.89	6.01	4.22	3.12	2.38	1.85	1.47
75.33	10.55	7.08	4.98	3.57	2.73	2.08
85.32	22.60	13.91	9.40	6.40	4.59	3.40

TABLE 5: Viscosities of aqueous solutions of lactic acid. Variation with concentration and temperature.

The correlation between viscosity and temperature could be demonstrated when the logarithms of the viscosities were plotted against the logarithms of the absolute temperatures. In this way the curves were transformed approximately into straight lines. The following expression is used:

# log(visc.) = A - B\*log(T),

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where viscosity in centipoises, temperature in K.

The coefficients for this expression are given in table 6.



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Figure 10 : Refractive index of lactic acid solutions as a function of concentration, at  $25^{\circ}$ C.

Lactic acid weight %	Α	В
9.16	14.93850	6.01758
24.35	16.78300	6.69890
45.48	19.56958	7.71428
64.89	23.66148	9.22637
75.33	27.79426	10.79120
85.32	32.48275	12.54945

TABLE 6: Correlation of temperature and viscosity for aqueous solutions of lactic acid.(log[visc.] = A - B\*log[T]; Viscosity [centipoises], T [K]).

The contents of intermolecular esters in lactic acid greatly influenced the viscosities of the solutions [6]. During the period in which the equilibrium was established after dilution of the acid, increasing viscosity was observed.

The measurements of the investigations recorded here were performed when the equilibrium was complete, as indicated by constant values of the viscosity.

#### 4.4 Refractivity.

The refractivities of aqueous solutions were determined by Vidler [5]. These solutions contained lactic acid in equilibrium with intermolecular esters, and the results are given in table 7 and illustrated in fig. 10. The measurements were performed by means of an Abbé refractometer, but the source of light was not stated, although probably a sodium lamp was used. The refractivity forms an essentially linear function of the concentration of lactic acid, the influence of the temperature is slight.

TABLE	7:	Refractivities	of	aqueous	solutions	of	lactic	acid,	as	a	function	of
concentr	atic	on and tempera	ture	).								

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Lactic acid weight %	Temperature	(°C)
	25	35
0	1.3325	1.3316
6.29	1.3390	1.3380
12.19	1.3448	1.3435
25.02	1.3586	1.3569
37.30	1.3718	1.3702
54.94	1.3909	1.3886
88.60	1.4244	1.4214

In fig. 10 the variation of the refractive index with concentration of lactic acid solutions at 25 °C is shown.





#### 4.5 Conductivity.

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Several determinations of the conductivity of aqueous solutions of lactic acid have been performed, generally for the purpose of obtaining the dissociation constant of the acid. Here the conductivity only is discussed.

In table 8 the specific as well as the equivalent conductivities are given for different lactic acid concentrations at 25 °C. These data are determined by Martin and Tartar [7] almost 55 years ago.

This investigation was performed with carefully purified lactic acid dissolved in conductivity water of specific conductivity not exceeding  $4.0.10^7$  mho/cm.

Fig. 11 shows the equivalent and specific conductivity as a function of the square root of the molar concentration of lactic acid at 25  $^{\circ}$ C. It demonstrates that there is an almost linear dependence between the specific conductivity and the square root of the concentration; at zero concentration the specific conductivity is practically equal to zero.

Fig. 11 also shows the equivalent conductivity as a function of the square root of the concentration. For small concentrations this curve ascends steeply. The equivalent conductivity at infinite dilution can therefore not be determined by means of this curve, but it can be determined by using the expression:

 $\Lambda_{\rm eq, \, lactric \, acid} = \Lambda_{\rm eq, \, HCl} - \Lambda_{\rm eq, \, KCl} + \Lambda_{\rm eq, \, K \, lactate}$ 

where  $\Lambda$  stands for the equivalent conductivities at infinite dilution of hydrochloric acid, potassium chloride and potassium lactate respectively. In this way the equivalent conductivity at infinite dilution was found to be 388.49 mho/eqv.

For higher concentrations the following expression for the equivalent conductivity was derived:

where c is the molar concentration of lactic acid and  $\alpha$  the ion concentration of the solution.



Figure 12: Equivalent conductivity of lactic acid solutions at infinite dilution, as a function of temperature.

Lactic acid		Conductivity		
Concentration c, (mol/l)	√c	Specific (mho/cm .10 <sup>3</sup> )	Equivalent (mho/eqv)	
0.0001606	0.0127	0.037	231.2	
0.0003817	0.0195	0.067	175.0	
0.0009213	0.0303	0.116	125.9	
0.002001	0.0447	0.182	90.91	
0.003543	0.0595	0.250	70.70	
0.005689	0.0754	0.324	56.91	
0.008266	0.0909	0.396	47.96	
0.01124	0.1061	0.468	41.60	
0.01756	0.1324	0.592	33.74	
0.02730	0.1652	0.744	27.31	
0.03283	0.1812	0.818	24.92	
0.04305	0.2075	0.943	21.87	
0.06338	0.2518	1.138	17.95	

TABLE 8: Specific and equivalent conductivities of lactic acid solutions at 25°C as a function of the molar concentration.

The same investigators also determined the equivalent conductivity at infinite dilution for the temperature range 0-50  $^{\circ}$ C, by means of the conductivities of hydrochloric acid, potassium chloride and potassium lactate (see previous page).

The values of these equivalent conductivities at infinite dilution are given in table 9. The variation of the conductivities at infinite dilution with temperature is illustrated in fig. 12.

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TABLE	9:	Equivalent	conductivity	of	aqueous	solutions	of	lactic	acid	at	infinite
dilution,	as	a function	of the temper	atu	re.						$\sim$

Temperature (°C)	Equivalent conductivity (mho/eqv)
0	241.9
10	298.2
20	357.3
25	388.5
30	415.8
40	468.0
50	517.4

The specific conductivities of more concentrated solutions of lactic acid have been determined for a series of solutions in which lactic acid was in equilibrium with lactoyllactic acid [5]. These conductivities are shown in table 10 and fig. 13.

TABLE 10: Specific conductivities of aqueous solutions of lactic acid at 25 °C as a function of the concentration. (Lactic acid in equilibrium with intermolecular esters.)

Lactic acid, weight %	Specific conductivity mho/cm*10 <sup>3</sup>
0	0.055
6.29	3.670
12.19	4.280
25.02	3.823
37.30	3.020
54.94	1.530
88.60	0.0567

It can be seen that the conductivity increases rapidly with the concentration until a maximum is reached at 12-15% lactic acid. Above that concentration the conductivity decreases, so that almost no conductivity can be observed for a solution containing about 90% by weight, calculated as lactic acid. It was suggested that this effect of concentration was largely due to increased viscosity of the solution, since the product of conductivity and viscosity did not show a maximum at 12-15% lactic acid; for the above mentioned product a maximum was found between 40% and 50% lactic acid. The small conductivity of concentrated lactic acid is probably due to the low concentration of water in connection with the very high viscosity.

#### 4.6 Surface tension.

Very little information is known about the surface tension of lactic acid solutions. A one molar lactic acid solution has a surface tension of 46.0 dyn/cm at 25  $^{\circ}$ C. Samples aged 20 and 38 years had surface tensions of 52.1 and 55.1 respectively. These higher values were considered to be caused by the age of the acid. The purity of the old samples was not examined, but they were described as pale yellow or orange-yellow liquids with a flat smell [8].

### 4.7 Dielectric constant.

Values of the dielectric constant of lactic acid have only been published about 90 years ago. The values were obtained without determination of the concentration.

The following values were found: 19.2 at 19°C for high frequency, 23 for low frequency and 20.90 at 15°C without indication of the frequency. [9]. The significance of these measurements must be regarded as doubtful.

# 4.8 Dissociation constant.

In 1889 the dissociation constant of lactic acid was estimated by Ostwald [10]. Ostwald's method consisted in determination of the conductivities of lactic acid in increasing dilutions. The dissociation constant was then calculated by the expression:  $\frac{h^{2}}{n} \frac{\left(\frac{\alpha}{\nu}\right)^{2}}{\frac{1-\alpha}{\nu}} = \frac{\alpha^{2}}{\frac{V(1-\alpha)}{\frac{1}{\nu}}}$ 

$$k = \alpha^2 / (1 - \alpha)^* 1 / v$$

where  $\alpha$  is the degree of dissociation and v is the molar volume of the acid. Ostwald found  $\alpha \rightarrow 1$ the mean value of k = 0.000138 at 25 °C corresponding to pK = 3.86, a value that doesn't differ much from the value, pK = 3.73 at 26 °C published by Lockwood, Yoder and Zienty in 1965 [11].

Martin and Tartar [7] also determined the dissociation of lactic acid from the measurements of conductivity.

Table 11 gives the dissociation constants and pKa of lactic acid at various concentrations at 25°C, and table 11a gives the dissociation constants and pKa of lactic acid at various temperatures.

Lactic acid (mol/l)	Dissociation constant	рКа
0.0001606	0.0001391	3.857
0.0009213	0.0001397	3.855
0.003543	0.0001383	3.859
0.008266	0.0001368	3.864
0.01124	0.0001367	3.864
0.01756	0.0001363	3.866
0.02730	0.0001354	3.868
0.03283	0.0001342	3.872
0.04305	0.0001337	3.874
0.06338	0.0001300	3.886

TABLE	11:	Dissociation	constants	and	рКа	of	lactic	acid	at	25	С,	at	various
concentr	ation	ns.											

Temperature (°C)	Dissociation constant	рК
0	0.0001317	3.880
5	0.0001339	3.873
10	0.0001356	3.868
15	0.0001375	3.862
20	0.0001389	3.857
25	0.0001387	3.858
30	0.0001378	3.861
40	0.0001339	3.873
45	0.0001309	3.883
50	0.0001274	3.895

TABLE 11a: Dissociation constants of lactic acid at various temperatures. ( $C_{\text{lactic acid}} = 0.002 \text{ mol}/1$ ).

# 5 LACTIC ACID AND OTHER SOLVENTS.

This section discusses the distribution of lactic acid between water and organic solvents. A large number of distribution coefficients are quoted in the tables. The investigation is closely connected with the more complicated problem of solvent extraction of lactic acid. The greater part of the distribution coefficients have been determined during the search for solvents that could be used for this purpose.

#### 5.1 Distribution coefficients.

Weiser [12] and Leonard, Peterson and Johnson [13] have determined a large number of distribution coefficients for lactic acid between water and organic solvents, in order to find suitable solvents for the extraction from crude acid.

Distribution coefficients (K) are recorded in the tables 12-16, where the solvents have been arranged according to their characteristic groups. The distribution coefficients are understood to be the proportion of the concentration in the aqueous phase to that in the organic phase. Concentrations have been quoted in g/100 ml. The distribution coefficients given in the tables are the apparent coefficients, calculated from the total concentrations in the phases,  $\propto 100$  irrespective of the fact that part of the acid in the aqueous phase is dissociated into a hydrogen ion and a lactate ion. This dissociation makes the distribution dependent on the concentration of lactic acid and on the pH in the aqueous phase.

All distribution coefficients given are based on pure anhydrous lactic acid; there's no lactoyllactic acid involved.

Solvent	T (°C)	C <sub>w</sub> (g/100ml)	K
Hexane	25	5.16	>100
Benzene	25	5.94	>100
Toluene	25	5.16	300
Cloroform	20	1.87	90
o-Dichlorobenzene	25	5.18	>100
Nitromethane	25	5.22	8.9
Nitroethane	25	5.69	23
Nitrobenzene	25	5.98	200

TABLE 12: Distribution on Hydrocarbons,	, Halogen compounds and Nitro compounds
(C <sub>w</sub> : concentration of lactic acid in water	phase).

Solvent	T (°C)	C <sub>w</sub> (g/100ml)	K
1-Butanol	25	3.12	1.40
2-Butanol	- 25	3.19	1.08
1-pentanol	20	4.59	2.29
1-Hexanol	25	4.79	3.20
1-Octanol	25	5.21	5.05
Cyclohexanol	25	3.95	1.73

# TABLE 13: Distribution on Alcohols.

# TABLE 14: Distribution on Ethers.

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Solvent	T (°C)	C <sub>w</sub> (g/100ml)	K
Ethyl ether	20	4.91	11.5
Isopropyl ether	25	16.21	33.4
Ethyl butyl ether	25	5.85	38
Butyl ether	25	5.97	73
Pentyl ether	28	2.20	100
Phenyl ether	25	6.02	500
Furan	26	3.04	80

# TABLE 15: Distribution on Aldehyden and Ketones.

Solvent	T ( <sup>°</sup> C)	C <sub>w</sub> (g/100ml)	K
2-Butanone	25	4.8	1.23
3-Pentanone	25	5.04	6.1
2-Heptanone	25	5.59	10.5
3-Heptanone	25	5.73	18
4-Heptanone	25	5.74	21

Solvent	T (°C)	C <sub>w</sub> (g/100ml)	K
Ethyl acetate	25	5.03	3.86
Propyl acetate	25	5.43	8.8
Butyl acetate	25	5.45	9.3
Pentyl acetate	26	2.80	8.8
Butyl lactate	25	4.26	1.76
Isobutyl lactate	28	1.61	1.86
Pentyl lactate	27	1.87	2.88
Amyl acetate	26	2.15	11.0
Diethyl carbonate	28	2.12	21
Tributyl phosphate	25	3.19	1.10

#### TABLE 16: Distribution on Esters.

The lowest distribution coefficients are found in connection with alcohols, ketones and esters. Bigger values are found with ethers and nitromethane. The distribution in connection with hydrocarbons, halogen compounds and higher nitro compounds is so disadvantageous that extraction with such solvents is unfeasible for practical purposes.

Through a series of homologous solvents the distribution coefficients generally increase with increasing molecular weight. From this it follows that solvents with low molecular weights are better for extraction processes than those with high molecular weights. But the miscibility of water and solvents is greatest for solvents of low molecular weight, so that comparatively more of the low-molecular-weight solvents is required in the extraction procedures. the result is that solvents of intermediate molecular weights are generally preferred.

Most of the distribution coefficients have been determined with lactic acid that had previously been heated for a long time in dilute aqueous solution in order to hydrolyse lactoyllactic acid. In some cases experiments have also been performed with lactic acid containing lactoyllactic acid. These distribution coefficients are generally substantially lower than those obtained with hydrolysed lactic acid.

## **TERNARY PHASE DIAGRAMS.**



Figure 14:  $T = 25^{\circ}C$ No.1: Lactic acid - water - 1-butanol. No.3: Lactic acid - water - 1-hexanol. No.4: Lactic acid - water - 1-octanol.







Figure 16:  $T = 25^{\circ}C$ No.1: Lactic acid - water - 2-butanone. No.2: Lactic acid - water - cyclohexanone. No.3: Lactic acid - water - isophorone.



Figure 17:  $T = 20^{\circ}C$ No.1: Lactic acid - water - butyl lactate. No.2: Lactic acid - water - ethyl acetate. No.3: Lactic acid - water - butyl acetate.

#### 5.2 Ternary phase diagrams and influence of concentration.

Some ternary phase diagrams are shown in fig. 14-18. Each of these figures illustrates a series of related solvents, namely alcohols, ketones, esters, and aromatic amines. There aren't any tie lines shown in these figures. Data for some typical tie lines are given in APPENDIX Zie A.[13]

The ternary phase diagrams are all of the same type, showing an area of two liquid phases in equilibrium for low concentrations of lactic acid. Increasing concentration of lactic acid increases the miscibility of water and solvent, so that the three components form one homogeneous phase, provided that sufficient lactic acid is in the system. This limiting concentration of lactic acid, amounts generally to 10-30%. Solvents with high distribution coefficients show the highest limiting concentrations. The highest value is found for isopropyl ether, about 70 %.

When solvent extraction of lactic acid is to be performed, the concentration of lactic acid in the system must kept below this limiting concentration. Simultaneously with the extraction of lactic acid, substantial amounts of water are transferred to the organic phase. After removal of the solvent this water remains with the lactic acid. The concentration of lactic acid in the product is therefore limited, so that concentration of the acid by evaporation of water is generally needed. The smallest contents of water in lactic acid obtained by extraction are found when sovents with high distribution coefficients are used. Such solvents show the largest areas of two liquid phases in equilibrium in the ternary diagrams. This means that crude lactic acid of high concentration can be treated with such solvents, but large amounts of those solvents are needed for the extraction procedure.

The influence of concentration on the distribution coefficients can be seen in table 17. Weiser [12] found slightly decreasing distribution coefficients with increasing concentration.

Dietzel and Schmitt [14] suggested that the influence of concentration was connected with the degree of dissociation of lactic acid in the aqueous phase. Within the concentration range where solvent extraction is generally applied, rather small effects are to be expected, as the degree of dissociation varies only from about 1.5% in 10% lactic acid by weight to about 3.5% in 1% lactic acid by weight. The investigation was carried out with ethyl ether.

With smaller concentrations in the aqueous phase, a weak acid relatively dissociates more. The smaller the concentration the more molecules dissociate. The resulting ions of this dissociation stay in the aqueous phase, so with decreasing concentration the distribution coefficient increases.
# TERNARY PHASE DIAGRAMS.



Figure 18: No.1: Lactic acid - water - aniline.  $(T = 20^{\circ}C)$ No.2: Lactic acid - water - o-toluidine.  $(T=30^{\circ}C)$ 

TABLE 17: Influence of the concentration on the distribution of lactic acid between water and ethyl ether.  $(T=21\degree C)$ .

 $(C_w = total \text{ concentration of lactic acid in aqueous phase.}$ 

 $\alpha$  = dissociation of lactic acid in aqueous phase.

K = distribution coefficient.)

C <sub>w</sub> (mol/l)	α (%)	К
0.215	2.75	12.7
0.490	1.87	11.5
0.985	1.34	11.1
1.150	1.24	11.1

#### 5.4 Critical solution temperatures.

A critical solution temperature for two compounds is defined as the temperature at which two partially miscible compounds become completely miscible. With aromatic hydrocarbons the following critical solutions were found [15].

TABLE 18: Critical solution temperatures of lactic acid and some aromatic hydrocarbons.

Compounds	Critical solution temp. (°C)
Lactic acid and benzene	66
Lactic acid and toluene	100
Lactic acid and m-xylene	124

The critical solution temperatures found were 11-15°C below the boiling point of the hydrocarbons in question at atmospheric pressure.

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#### 5.4 Solubility.

The intensive study of distribution coefficients has revealed that lactic acid is completely miscible with a great number of solvents, including water, ethanol and ethyl ether. Very little information is available about solubility in solvents that are not completely miscible with lactic acid. Francis [16] found that lactic acid is not complete miscible with hydrocarbons like hexane but quantitative information was not given.

#### 6 PHYSICAL PROPERTIES OF INTERMOLECULAR ESTERS OF LACTIC ACID AND DERIVATIVES.

In the preceding chapters of this paper it was established that lactic acid in equilibrium always contains lactoyllactic acid, polylactic acid and a little dilactide. There is very little known about the physical properties of these compounds. But what is known is given here. The next sections deal with the physical properties of these compounds and their derivatives.

#### 6.1 Lactoyllactic acid and derivatives.

Lactoyllactic acid is of the form:

The dissociation constant of lactoyllactic acid was first determined by Ringer and Skrabal [17], who prepared a solution of sodium lactoyllactate by rapid titration of a weighed quantity of dilactide in acetone, with aqueous sodium hydroxide; to the titrated solution was added the same weight of dilactide dissolved in acetone; after about 16 hours this was hydrolysed quantitatively to lactoyllactic acid, so that the solution now contained equal quantities of lactoyllactic acid and its sodium salt. This solution showed pH = 3.05, corresponding to the dissociation constant 0.00099. This value is about 7 times the dissociation constant of lactic acid (0.000138) at T=20°C, and lactoyllactic acid is thus considerably stronger than lactic acid.

Information about salts of lactoyllactic acid is limited, because they are comparatively unstable.

#### Esters of lactoyllactic acid.

Esters of lactoyllactic acid are of the form:

Several esters of lactoyllactic acid are known. These esters are considerably more stable than the acid and its salts.

R-lactoyl-lactate	Pressure	(mmHg)	
	0.1	1.0	10
Methyl	44	73	111
Ethyl	48	77	116
Propyl	54	85	124
Butyl	63	94	134
sec-Butyl	56	86	126
Hexyl	79	111	153
Octyl	97	131	176
1-Methylheptyl	89	122	164
Allyl	58	88	128

TABLE 21: Boiling points of esters of lactoyllactic acid at various pressures. (Temperature, °C).

In table 22 the density, the refraction index, the viscosity, as well as the solubility in water of esters of lactoyllactic acid are given. [18]

R-lactoyl- lactate	Density (g/ml)	Refraction index	Viscosity (cp)	Solubility in water (g/100ml)
Methyl	1.1609	1.4314	28.14	00
Ethyl	1.1136	1.4292	17.09	~
Propyl	1.0764	1.4304	14.20	2.2
Butyl	1.0622	1.4329	17.06	0.92
sec-Butyl	1.0528	1.4295	20.10	1.16
Hexyl	1.0280	1.4362	21.64	0.08
Octyl	1.0042	1.4396	26.57	< 0.01
Allyl	1.1172	1.4448	18.60	4.2

TABLE 22: Other physical properties of esters of lactoyllactic acid.  $T=20\degree C$ 

Also from acetates of esters of lactoyllactic acid some physical properties are known [19]. The structure of acetates of esters of lactoyllactic acid is:

> CH3 CH3 I CH3CO-O-CH-CO-O-CH-CO-O-R

In table 23 boiling points are given at pressures of 1 and 10 mmHg.

TABLE 23: Boiling points (°C) of acetates of esters of lactoyllactic acid.

R	Pressure	(mmHg)
	1	10
2-Butoxyethyl	129	156
2-(2-Butoxyethoxy)ethyl	167	200
Tetrahydrofurfuryl	138	170
2-(2-Chloroethoxy)ethyl	161	194

Some physical properties are shown in table 24.

TABLE 24: Density and refraction of acetates of esters of lactoyllactic acid. T=20°C

R	Density	Refraction
	(g/ml)	
2-Butoxyethyl	1.0705	1.4340
2-(2-Butoxyethoxy)ethyl	1.0785	1.4383
Tetrahydrofurfuryl	1.1556	1.4488
2-(2-Chloroethoxy)ethyl	1.2008	1.4416

CH3 - C - CH3

#### 6.2 Dilactide.

Dilactide is the bimolecular cyclic ester of lactic acid. The stucture is:



Dilactide exists as three different configurations depending on the configurations of the lactic acid from which the molecule is formed.



Each of the molecules (I) and (II) is formed from two identical molecules of lactic acid, D and L respectively; (I) and (II) are mirror images and therefore enantiomeric. Molecule (III) is formed from one molecule D- and one molecule of L-lactic acid; this molecule has a centre of symmetry, and it is therefore an optically inactive form. Dilactide prepared from racemic lactic acid must contain equal quantities of (I) and (II), together with an unknown quantity of (III).

The melting point of racemic dilactide ranges from  $120^{\circ}$ C to  $128^{\circ}$ C [17]. For the optically active dilactides melting points at 95°C are found [20].

The boiling point of dilactide at atmospheric pressure is  $255^{\circ}$ C. Dilactide is very soluble in acetone and almost insoluble in water.

L(-)Dilactide shows very strong rotation of polarized light; the specific rotation of a solution containing 1.1665 g/100ml in benzene was -298° for sodium light at 18°C [20].

#### 6.3 Polylactic acid.

From polylactic acid not much is known, but of some esters of polylactic acids some physical properties are known [1].

The structure of an ester of polylactic acid is:



Table 25 gives some data of physical properties of some esters of polylactic acids.

TABLE 25: Density, Refraction and kinematic viscosity of esters of polylactic acid. T=20 °C

(Approximate mean number of lactic acid units: n=3 per molecule.)

R	Density (g/ml)	Refraction index	Viscosity (Centistokes)
Methyl	1.2043	1.4430	1 <b>76</b>
Ethyl	1.2047	1.4460	1094
Butyl	1.1003	1.4374	63
Octyl	1.0517	1.4427	89
1-Methylheptyl	1.0197	1.4418	222.
2-Ethylhexyl	1.0821	1.4444	241
Benzyl	1.1843	1.4890	545
2-Ethoxyethyl	1.1904	1.4471	2721
2-Butoxyethyl	1.1225	1.4420	137
2-Phenoxyethyl	1.1998	1.4919	2598

#### 6.4 Polylactide.

Polylactide is the generally accepted term for highly polymeric polylactic acids. Such polymers are always obtained by polymerization of dilactide. The properties of optically inactive and optically active materials are very different.

The variation of the properties is due to the different configurations.

The solid polymer has a crystalline structure. Optically active polylactide has a helical conformation. This conformation, which has 3 1/3 monomers per turn, is shown in fig. 19.



Fig. 19: Helical conformation of poly-L-lactide.

6.4.1 Optically inactive polylactide.

Optically inactive polylactides are soluble in all commom solvents except petroleum and water. Fractionation of products of different degrees of polymerization can be performed by dissolution in ethyl ether and precipitation with petroleum. The products are resinous and generally sticky or brittle at room temperature, depending on their mean molecule weights. The softening points also depend on the degree of polymerization: products of mean degrees of polymerization about 10 and about 60 soften at 40°C and 82°C respectively. [21]

The lactic acid units form of optically inactive polylactides are either L- or D-forms, which are distributed at random along the main chain of the molecule; Such products are called atactic polymers, and their properties are influenced by the fact that every individual molecule has its own configuration depending on the sequence in which the two different forms occur. Atactic polylactides cannot be obtained with a degree of polymerization greater than about 60, corresponding to a mean molecular weight of about 4000.

#### 6.4.2 Optically active polylactide.

Polylactides can also be prepared from optically active dilactide. The properties of these polymers differ considerably from the properties of the atactic polymers. This is caused by the uniformity of configuration.

The softening point of poly-L-lactides are considerably higher than those of racemic (and atactic) polylactides: they may be as high as 171-176°C. Whereas the optically inactive form is comparatively soluble in most organic solvents, the optically active are slightly soluble. good solubility is only found in chlorinated hydrocarbons, chloroform and trichloroethylene. Optically active polylactides are soluble in boiling toluene provided that the degree of polymerization is not too high. The degree of polymerization can be very high, but no definite limit has been published. [21]

#### 7 PHYSICAL PROPERTIES OF ESTERS OF LACTIC ACID.

Since lactic acid is an alcohol as well as an acid it can form two types of esters. This chapter describes esters with alcohols, and the compounds resulting possess the alcohol group unchanged in the lactic acid part of the molecule. The structure of an ester of lactic acid is:

#### CH<sub>3</sub> - CH(OH) - COOR

#### 7.1 Melting points of alkyl lactates.

The majority of all known lactate esters are liquid at room temperature or low melting solids. Melting points are given in table 26. [22]

### TABLE 26: Melting points (°C) of alkyl lactates.

Lactate	Melting point (°C)
Propyl	-40
Butyl	-28
Pentyl	-22
Hexyl	-22
Octyl	-4
Decyl	8
Dodecyl	25
Tetradecyl	31
Hexadecyl	41

7.2 Solubilities of alkyl lactates. The presence of the free alcohol group causes considerably higher solubilities in water than the presence of the free alcohol group causes considerably higher solubilities in water than is the case for esters of carboxylic acids. Methyl, ethyl, propyl and isopropyl esters of lactic acid are miscible with water. Many esters of higher aliphatic esters are partially miscible with water, but the solubilities have only been determined in a few cases. [22]

#### TABLE 27: Solubilities of alkyl lactates in water, T=25°C

Lactate	Solubility (g/100ml)
Methyl	miscible
Ethyl	miscible
Propyl	miscible
Isopropyl	miscible
Butyl	4.36
Pentyl	1.00
Hexyl	0.27
Octyl	0.08
Decyl	0.02
Dodecyl	0.01

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Many lactate esters are also miscible with or very soluble in organic solvents, but there's hardly any information about this.

#### 7.3 Distribution coefficient.

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Only one distribution coefficient for a lactate ester between water and another solvent has been found.

The distribution coefficient of methyl lactate between water and ethyl ether is K = 2.70 for a system containing 14.5% methyl lactate by weight at 10°C. [23]

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#### 7.4 Boiling points of alkyl lactates.

Lactate esters are generally purified by distillation. Lower esters can be distilled at atmospheric pressure. Boiling points are given in table 28. [22]

Lactate		Pressure	(mmHg)		
	0.1	1.0	10	100	760
Methyl	-	-	42	87	145
Ethyl	-	-	51	94	154
Propyl		-	61	108	169
Butyl		40	75	125	187
Pentyl		52	89	140	206
Hexyl	34	64	103	155	221
Octyl	55	87	128	184	255
Decyl	76	109	152	211	283
Dodecyl	94	129	174	236	310
Tetradecyl	115	151	198	261	335
Hexadecyl	132	170	219	283	-

TABLE 28: Boiling points (°C) of alkyl lactates.

Optically active lactates show the same boiling points as esters of racemic lactic acid. Exceptions from this rule are esters of optically active alcohols. The molecules of such esters can be composed of a lactic acid molecule and an alcohol having the same sign or opposite sign of the optical rotations. These two possible forms are diastereoisomeric, and they can therefore differ significantly in physical properties. The differences are, however, generally small. [22]

# 7.5 Flash points.

In table 29 flash points of some alkyl lactates are given. The experiments are done in a closed cup. [24]

TABLE 29: Flash points (°C) of alkyl lactates.

Lactate	Flash point (°C)	
Methyl	49	
Ethyl	46	
Butyl	71	
Isopentyl	79	



Figure 20: Densities of optically active and racemic methyl lactate at various temperatures.

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#### 7.6 Densities of alkyl lactates.

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Densities of methyl lactate [25] and ethyl lactate [26] are determined at various temperatures. The results are quoted in table 30 and 31.

Densities of optically active methyl lactate as well as racemic methyl lactate have been determined. No significant differences can be detected between the values obtained with optically active ester and those obtained with racemic ester (see Fig.20).

The values given in the tables are average values because different samples of the same ester show considerably variation in the observed values.

Figure 20 shows the densities of methyl lactate at various temperatures.

Temperature	Densities	(g/ml)
( <sup>°</sup> C)	Optically active	Racemic
-76	1.2042	-
- 8.6	1.1205	-
10	-	1.1005
16.7	1.0971	-
20	-	1.0915
25	-	1.0895
30	-	1.0796
40	_	1.0694
50	-	1.0584
56	1.0518	-
60	-	1.0474
78.8	1.0256	-
80	_	1.0243
86.7	1.0048	-
125	0.9725	-

#### TABLE 30: Densities of methyl lactate at various temperatures.



Figure 21: Densities of ethyl lactate at various temperatures.

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Temperature (°C)	Densities (g/ml)	
0	1.0550	
10	1.0405	
17.3	1.0379	
20	1.0348	
25	1.0299	
30	1.0214	
38.4	1.0157	
40	1.0102	
50	1.0031	
55.4	0.9972	
60	0.9878	
70	0.9808	
81.2	0.9680	
99.8	0.9463	

TABLE 31: Densities of ethyl lactate at various temperatures.

In table 31 the densities of ethyl lactate at various temperatures are given. They are also shown in figure 21.

#### 7.7 Refractivities of methyl lactates.

Also refractivities of methyl lactate at various temperatures have been determined. [27] Values are reported in table 32.

Troupe and Kobe have determined the refractivities of aqueous solutions of methyl lactates a function of the concentration [28]. This variation is shown in table 33 and in figure 22.



Figure 22: Refractivities of aqueous solutions of methyl lactate as a function of concentration, at  $25^{\circ}$ C.

Temperature (°C)	Refractive index
10	1.4183
15	1.4162
20	1.4141
25	1.4120
40	1.4053

TABLE 32: Refractivities of methyl lactate at various temperatures.

TABLE 33: Refractivities of aqueous solutions of methyl lactate at 25 °C.

Methyl lactate weight %	Refractive index	
0.00	1.3326	
15.75	1.3471	
33.30	1.3625	
50.00	1.3775	
67.00	1.3916	
71.00	1.3947	
79.00	1.4004	
92.75	1.4084	
95.50	1.4098	
100.00	1.4121	

#### 7.8 Viscosities of methyl lactate and ethyl lactate.

Viscosities have been determined for methyl lactate and ethyl lactate [29]. The results are shown in table 34. The viscosities are comparable with that of 1-butanol, and the esters are more viscous than simple esters such as ethyl acetate.

Temperature (°C)	Methyl lactate	Ethyl lactate
10	<u>-</u>	3.681
20	-	2.681
30	2.62	2.042
40	1.97	1.608
50	1.56	-
60	1.25	1.079
70	1.02	-
80	0.84	0.780

TABLE 34: Viscosities of methyl lactate and ethyl lactate at various temperatures. (Viscosities in centipoises)

#### 7.9 Surface tension.

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Surface tensions have been determined for several normal alkyl lactates [30]. The variation with temperature has been investigated in the case of ethyl lactate [31]. The results are recorded in tables 35 and 36.

TABLE 35: Surface tensions of normal alkyl lactates at room temperature.

Lactate	Surface Tension (dyn/cm)
Ethyl lactate	29.20
Propyl lactate	29.00
Butyl lactate	28.80
Hexyl lactate	28.86
Heptyl lactate	28.88

Temperature (°C)	Surface tension (dyn/cm)
15	29.45
40	26.99
45.2	26.31
78.4	22.96
108.4	20.08

TABLE 36: Surface tensions of ethyl lactate at various temperatures.

#### 7.10 Optical rotation.

In the articles published about the physical properties of alkyl lactates it is never mentioned whether or not optically active or optically inactive ester is used. It's possible that the results obtained with optically active esters have been mixed with results obtained with optically inactive ester.

In this section the optical rotations of lactate esters are discussed. [32] The sign of rotation is almost always the opposite of the sign of rotation of the lactic acid contained in the molecule. In table 37 the signs corresponding to esters belonging to the L-series are given. A sodium light is used, and the values are estimated for the pure compounds, no solvent is involved. In the results found for esters of the D-series the sign is changed accordingly.

TABLE 37:	Specific rotati	ons of esters	of L(+	)Lactic acid	at 20°	C.
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L(-)Lactate	$\left[\alpha\right]_{D}^{20}$
Methyl	- 8.26°
Ethyl	-11.32°
Propyl	-13.21°
Butyl	-13.45°
Isobutyl	-15.18°

tert-Butyl	- 9.45°
Pentyl	-12.57°
Hexyl	-11.86°
Heptyl	-10.96°
Octyl	- 9.36°
Nonzyl	- 9.20°





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A = Sodium lactate, B = Potassium lactate, C = Ammonium lactate.

#### 8 PHYSICAL PROPERTIES OF ALKALI AND AMMONIUM LACTATES.

Solutions of alkali and ammonium lactates have been investigated over a wide concentration range. Dietz, Degering and Schopmeyer [33] determined the physical properties of aqueous solutions of sodium lactate, potassium lactate and ammonium lactate. Table 38-42 and figures 23-27 show the results.

Concentration	Density	(g/ml)	
% by weight	Sodium Lactate	Potassium Lactate	Ammonium Lactate
0	0.9971	0.9971	0.9971
5	1.0225	1.0217	1.0155
10	1.0511	1.0465	1.0270
15	-		1.0385
20	1.1002	1.0985	1.0531
30	1.1542	1.1528	1.0819
40	1.2078	1.2102	1.1081
50	1.2629	1.2699	1.1334
60	1.3131	1.3307	1.1571
70	1.3717	1.3928	1.1808
80	1.4320	1.4300	1.2008

TABLE 38: Densities of aqueous solutions of	alkali and ammonium l	actates at 25°C
TABLE 38: Densities of aqueous solutions of	alkali and ammonium l	actates at 25 C



Figure 24: Refractivities of aqueous solutions of lactates as a function of concentration, at 25°C.

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A = Sodium lactate, B = Ammonium lactate, C = Potassium lactate.



Figure 25: Boiling points of aqueous solutions of lactates as a function of concentration, at atmospheric pressure.

A = Sodium lactate, B = Potassium lactate, C = Ammonium lactate.

Concentration	Refractivity	index	
% by weight	Sodium Lactate	Potassium lactate	Ammonium Lactate
0	1.3329	1.3329	1.3329
10	1.3473	1.3456	1.3470
20	1.3623	1.3589	-
30	1.3778	1.3729	1.3761
50	1.4078	1.4018	1.4059
70	1.4353	1.4306	1.4351

TABLE 39: Refractivities of aqueous solutions of alkali and ammonium lactates at 25°C, variation with concentration.

TABLE 40: Boiling points (°C) of aqueous solutions of alkali and ammonium lactates, at atmospheric pressure. Variation with concentration.

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Concentration	Boiling	Point (°C)	(P=742mmHg)
% by weight	Sodium Lactate	Potassium Lactate	Ammonium Lactate
0	99.33	99.33	99.33
5	99.75	99.68	99.53
10	100.11	100.13	99.93
20	101.43	101.35	
30	103.31	103.11	101.91
40	105.53	105.67	_
50	108.73	109.35	105.49
60	112.88	114.58	107.91
70	119.43	123.12	111.93
80	- ,	-	117.81

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Figure 26: Freezing points of aqueous solutions of lactates as a function of concentration.

A = Sodium lactate, B = Potassium lactate, C = Ammonium lactate



Figure 27: Viscosity of aqueous solutios of lactates as a function of concentration, at 25 °C.

A = Sodium lactate, B = Potassium lactate, C = Ammonium lactate.

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Concentration	Freezing	Point (°C)	
% by weight	Sodium Lactate	Potassium Lactate	Ammonium Lactate
0	0.0	0.0	0.0
5	-2.2	-1.6	-1.9
10	-4.1	-3.7	-3.3
20	-9.7	-8.6	-
30	-18.2	-16.1	-14.8
40	-32.5	-28.1	-
50	-	-51.0	-
60	-	_	-51.8

TABLE 41: Freezing points	of aqueous	solutions o	of alkali	and	ammonium	lactates,
variation with concentration.						

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TABLE 42: Viscosity of aqueous solutions of alkali and ammonium lactates at 25°C, variation with concentration.

Concentration	Viscosity	(Centipoises)		
% by weight	Sodium Lactate	Potassium lactate	Ammonium lactate	
0	0.894	0.894	0.894	
5	1.060	0.999	1.017	
10	1.240	1.128	1.073	
20	2.038	1.490	-	
30	3.638	2.105	2.748	
40	7.291	3.289	-	
50	17.979	5.492	5.410	
60	55.063	11.320	10.103	
70	379.85	33.456	22.573	



Figure 28: Ultraviolet adsorption of A: Lactic acid, B: Sodium lactate, C: Ethyl lactate.



Figure 29: Infrared absorption of lactic acid.

#### 9 SPECTRA.

This chapter discusses various spectra of lactic acid and some of its derivatives; whenever possible additional information that can be deduced from the spectra has been included. Three types of spectra will be discussed:

- 1. Ultraviolet spectra.
- 2. Infrared spectra.
- 3. Microwave spectra.

#### 9.1 Ultraviolet spectra.

The first measurements of the ultraviolet absorption by lactic acid have been done in 1913 by Bielecki and Henry [34]. They examined a commercial sample of 1.21 g/ml, for which they found slightly increasing extinction until about 250 nm. Complete extinction was observed at 226 nm. The article did not contain information about the solvent and concentrations used in the experiments.

Also Levene and Rothen [35] measured the ultraviolet spectrum of lactic acid. They found increasing ultraviolet absorption in the region 250 nm to 210 nm. The absorption at shorter wavelengths was constant, but the increasing part of the curve had a form indicating that maximum absorption should be found at 215 nm. The ultraviolet absorption spectra of sodium lactate and ethyl lactate were similar, but with maximum absorptions at 200 nm. These absorption curves are shown in figure 28.

It was not mentioned whether an optical active compound, for recording the spectra was used or not.

#### 9.2 Infrared spectra.

A complete recording of the infrared spectrum of lactic acid has been published by Mücke, Geppert and Kipke [36]. This spectrum is shown in figure 29, and table 42 contains a list of absorption bands that have been observed in this investigation.

A spectrum obtained by Dolinsky and Wilson [37] show some differences; two of the bands that appear in figure 29 at 2.9 10<sup>6</sup>m and 9.2 10<sup>6</sup>m are clearly resolved, and in the region above 11 10<sup>-6</sup>m the bands at 12.25 10<sup>-6</sup>m and 13.55 10<sup>-6</sup>m have been replaced by bands at 11.9 10<sup>-6</sup>m and 13.0 10<sup>-6</sup>m. They don't explain these differences because they don't know.

Absorption Ba	unds <i>a</i>	Assignments		
μm	cm <sup>-1</sup>			
1.2	8300			
1.49	670 <b>0</b>	overtone		
1.7 - 1.75	<b>5900-57</b> 00	Ь		
1.94	5155	combined vibration		
2.76 - 2.78	3620-3605	free OH c		
2.81 - 2.84	3565-3470	bound OH c		
2.90	3448	ОН, ν		
3.28	3050	bound OH		
3.36 - 3.39	2980-2950	CH3, 1		
3.71 - 3.97	2700 - 2520	COOH		
5.0	2000	b		
5.70 - 5.83	1755-1720	С=0, г		
6.90	1450	CH <sub>3</sub>		
7.09	1410	OH		
7.32	1365	$CH_3, \delta$		
7.57	1320	≡CH		
7.81	1280	C=0 (?)		
8.07-8.30	1230-1205	COOH		
8.89-8.95	1125-1117	C-O (alcohol), v		
9.20	1087			
9.57-9.62	1045-1040	ОН, δ		
10.87-10.91	920-917	ΟΗ, γ		
12.13-12.25	825-816	•		
13.37-13.55	748-738			

#### TABLE 43: Infrared absorption bands of lactic acid.

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Several of the frequencies mentioned have been assigned to definite elements of configurations, or to definite vibrations of the molecule, and from these considerations it war concluded that lactic acid in solution occurs as intermolecular-association compounds connected by hydrogen bonds. It was found that neighbouring molecules of lactic acid were attached either by two hydroxyl groups or by two carboxyl groups, so that the final conclusion was that the association could best be explained by supposing the structure shown in figure 30.

Physical properties of lactic acid and derivatives.



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Figure 30: Stucture of lactic acid in solution.

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#### 9.3 Microwave spectra.

The microwave spectrum of L(+)-lactic acid has been identified with aid of double resonance techniques by van Eijck [38]. From this spectrum it follows that the molecule shows a hydrogen bond from the  $\alpha$ -hydroxyl group to the carbonyl oxygen atom. Figure 31 shows a projection of the L(+)-lactic acid molecule.



Fig. 31: Projection of the L(+)-lactic acid molecule.

# APPENDIX: Tie-lines of ternary phase diagrams of lactic acid with water and an organic solvent.

#### Tie-line data for systems: Lactic acid-Water-Organic solvent.

All concentrations are percent by weight.

LA = lactic acid.

W = Water.

S = Solvent.

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## System: Lactic Acid-Water-Alcohol (T=25°C)

Solvent	Aq.	Phase		Org.	Phase	
	LA	w	S	· LA	W	S
1-butanol	0.0	92.8	7.2	0.0	19.9	80.1
	5.2	89.5	7.6	4.6	24.2	71.2
	10.5	79.6	9.9	9.9	30.2	59.9
1-Octanol	0.0	100.0	0.0	0.0	4.7	95.3
	16.5	87.7	0.0	4.5	5.9	89.6
	36.7	63.3	0.0	12.9	8.1	79.0
	53.5	45.7	0.8	27.1	12.9	60.0

System: Lactic Acid-Water-Ethers (T=20°C)

Solvent	Aq.	Phase		Org.	Phase	
	LA	W	S	LA	W	S
Isopropyl	0.0	99.0	1.0	0.0	0.5	99.5
ether	31.5	67.3	1.2	3.3	0.6	96.1
	70.0	20.0	10.0	8.0	0.7	91.3
Ethyl	0.0	93.7	6.3	0.0	1.3	98.7
ether	16.5	76.0	7.5	5.4	2.0	92.6
	34.8	53.0	12.0	11.4	3.0	85.6
	43.7	32.0	24.0	21.5	6.5	72.0

Solvent	Aq.	Phase		Org.	Phase	
	LA	W	S	LA	W	S
2-	0.0	74.5	25.5	0.0	12.4	87.6
Butanone	2.7	70.2	27.1	2.0	16.1	81.9
	5.4	58.9	35.7	4.6	24.2	71.2
Cyclo-	0.0	91.4	8.6	0.0	6.6	93.4
hexanone	4.9	85.6	9.5	2.9	8.1	89.0
	11.0	77.8	11.2	7.3	11.3	81.4
	16.5	65.2	18.3	12.4	17.9	69.7

# System: Lactic Acid-Water-Ketones (T=25°C)

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System: Lactic Acid-Water-Esters (T=20°C)

Solvent	Aq.	Phase		Org.	Phase	
	LA	W	S	LA	W	S
Ethyl	0.0	92.6	7.4	0.0	3.0	97.0
acetate	6.6	85.0	8.4	3.2	4.0	92.8
	25.7	59.3	15.0	18.1	9.9	72.0
Butyl	0.0	99.3	0.7	0.0	1.4	98.6
acetate	7.0	92.0	1.0	3.0	2.0	95.0
	29.6	69.4	1.0	8.7	2.8	88.5
	51.5	42.0	6.5	12.2	3.3	84.5

Solvent	Aq.	Phase		Org.	Phase	
	LA	W	S	LA	W	S
Aniline	0.0	96.4	3.6	0.0	5.2	94.8
$T=20^{\circ}C$	9.4	76.5	14.1	2.8	9.0	88.2
	12.8	66.0	21.0	8.2	20.0	72.0
0-	0.0	98.3	1.7	0.0	2.7	97.3
Toluidine	7.0	85.0	8.0	1.3	5.0	94.0
$T=30^{\circ}C$	12.2	75.0	12.0	3.5	5.5	91.0
	15.6	64.0	20.0	6.4	10.0	84.0

# System: Lactic Acid-Water-Aromatic Amines
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