Dissociation equilibrium with Cobra4 (Item No.: P3030960)

Curricular Relevance

Area of Expertise: Chemistry

Education Level: University

Topic: General Chemistry

Subtopic: Solutions and Mixtures

Experiment: Dissociation equilibrium with Cobra4

Difficulty	Preparation Time	Execution Time	Recommended Group Size
Difficult	10 Minutes	20 Minutes	2 Students

Additional Requirements:

- PC with USB interface, Windows XP or higher
- Precision balance, 620 g / 0.001 g

Experiment Variations:

Keywords:

true and potential electrolytet, strong and weak acids, law of mass action, Henderson-Hasselbalch equation, dissociation constant and p K_a value, substituent effect, potentiometry

Overview

Short description

Related Topics

True and potential electrolytes, strong and weak acids, law of mass action, Henderson-Hasselbalch equation, dissociation constant and p*K*a value, substituent effect, potentiometry.

Principle

Carboxylic acids are potential electrolytes which exist in a weakly dissociated condition in aqueous solutions. The location of the dissociation equilibrium is quantitatively described by the K_a or pK_a value which can be determined with potentiometric measurements.

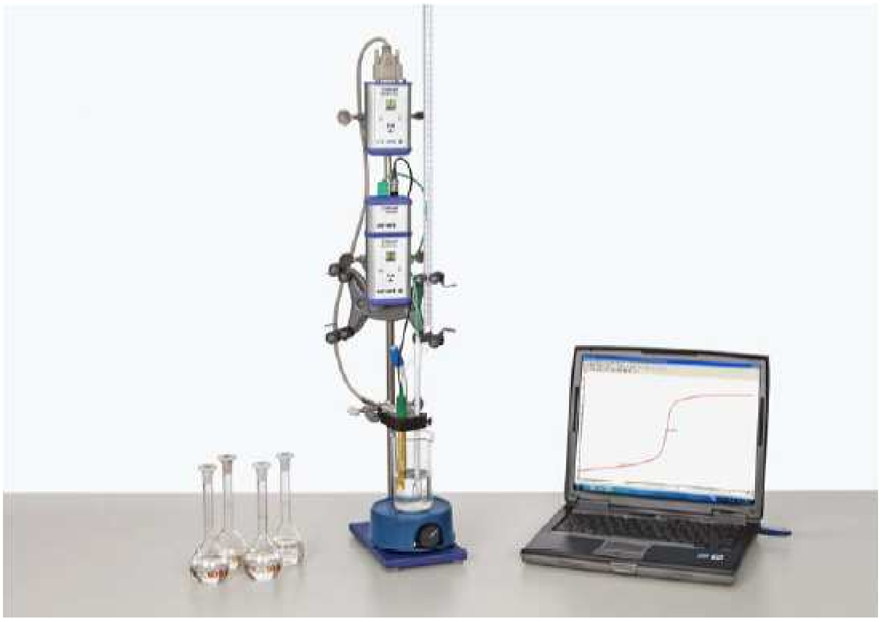

Fig. 1: Experimental setup.

Safety instructions

N-butyric acid
H302: Harmful if swallowed.
H314: Causes severe skin burns and eye damage.
P260: Do not breathe dust/fumes/gas/mist/vapours/spray.
P280: Wear protective gloves/protective clothing/eye protection/face protection.

Monochloracetic acid
H301: Toxic if swallowed
H311: Toxic in contact with skin
H400: Very toxic to aquatic life
P261: Avoid breathing dust/fumes/gas/mist/vapours/spray.
P273: Avoid release to the environment.

Lactic acid
H315: Causes skin irritation.
H318: Causes serious eye damage.
P313: Get medical advice/attention.

Acetic acid
H226: Flammable liquid and vapour.
H314: Causes severe skin burns and eye damage
P280: Wear protective gloves/protective clothing/eye protection/face protection.

Propionic acid
H226: Flammable liquid and vapour.
H314: Causes severe skin burns and eye damage.
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P280: Wear protective gloves/protective clothing/eye protection/face protection.

Caustic soda solution
H290: May be corrosive to metals.
P280: Wear protective gloves/protective clothing/eye protection/face protection.

Equipment

Position No.	Material	Order No.	Quantity
1	Cobra4 Sensor-Unit Chemistry	12630-00	1
2	curricuLAB measureLAB	14580-61	1
3	Immersion probe NiCr-Ni, teflon, 300 °C	13615-05	1
4	Rubber stopper,d=18/14mm, 1 hole	39254-01	1
5	Magnetic stirrer without heating, 3 ltr., 230 V	35761-99	1
6	Magnetic stirring bar 15 mm, cylindrical	46299-01	1
7	Beaker, high, BORO 3.3, 50 ml	46025-00	2
8	Beaker, high, BORO 3.3, 150 ml	46032-00	1
9	Beaker, high, BORO 3.3, 250 ml	46027-00	1
10	Volumetric flask 100 ml, IGJ12/21	36548-00	6
11	Volumetric pipette, 5 ml	36577-00	6
12	Pipettor	36592-00	1
13	Pipette dish	36589-00	1
14	Pasteur pipettes, 250 pcs	36590-00	1
15	Rubber caps, 10 pcs	39275-03	1
16	Microspoon, steel	33393-00	1
17	Wash bottle, plastic, 500 ml	33931-00	1
18	Buffer solution, pH 4.62 1000 ml	30280-70	1
19	Buffer solution, pH 9 1000 ml	30289-70	1
20	Acetic acid 99...100%, pure 1 l	31301-70	1
21	Monochloroacetic acid 100 g	30060-10	1
22	Propionic acid, 500 ml	31753-50	1
23	N-butyric acid 100 ml	30047-10	1
24	Lactic acid 100 ml	30264-10	1
25	Caustic soda sol.,0.1M 1000 ml	48328-70	1
26	Water, distilled 5 l	31246-81	1
27	Cobra4 Wireless/USB-Link incl. USB cable	12601-10	2
28	pH-electrode, plastic body, gel, BNC	46265-15	1
29	Holder for Cobra4 with support rod	12680-00	2
30	Cobra4 Sensor-Unit Drop Counter	12636-00	1
31	Right angle boss-head clamp	37697-00	3
32	Retort stand, h = 750 mm	37694-00	1
33	USB charger for Cobra4 Mobile-Link 2 and Wireless/USB-Link	07932-99	2
34	Burette clamp, roller mount., 2 pl.	37720-00	1
35	Burette, lateral stopcock, Schellbach, 25 ml	36506-01	1

Tasks

1. Measure the alteration of the pH value during a titration of approximately 0.1 molar aqueous solutions of formic acid, acetic acid, monochloracetic acid, propionic acid, butyric acid and lactic acid with a 0.1 molar sodium hydroxide solution at constant temperature using the Cobra4 system.
2. From the neutralisation curves read the pK_a values of the acids and compare them.

Set-up and procedure

Set-up

Set-up

- Set up the experiment as shown in Fig. 1.
- Combine the Cobra4 Sensor Unit Chemistry and the Cobra4 Drop Counter with the Cobra4 Wireless-Links.
- Attach them to the retort stand with the holders for Cobra4 and right angle clamps.
- Connect the pH electrode to the pH input of the Cobra4 Sensor Unit Chemistry and the temperature probe to temperature input T1.
- Start the PC and connect the Cobra4 Wireless Manager with a USB socket of the computer.
- Switch on the Cobra4 Wireless/USB-Link ( ). Connect your computer via WiFi with the Wireless/USB-link (maximum range 50m) or attach the Cobra4 device to the computer with the USB cable.
- Start the software . The Cobra4 measuring device will be automatically detected.
- Boot the experiment “Dissociation equilibrium with Cobra4” (Load experiment). The measurement parameters for this experiment are loaded now.

Calibrate the pH electrode:
To do so, use the buffer tablets for the two pH values to perform two-point calibrations.
If the electrode has already been calibrated recently, a new calibration is not necessary.

Go to settings and select pH Sensor. Click on Calibration (Fig. 2) and perform a 2-point calibration by using two buffer solutions, e.g. pH 4.0 and pH 10.0 (Fig. 3).

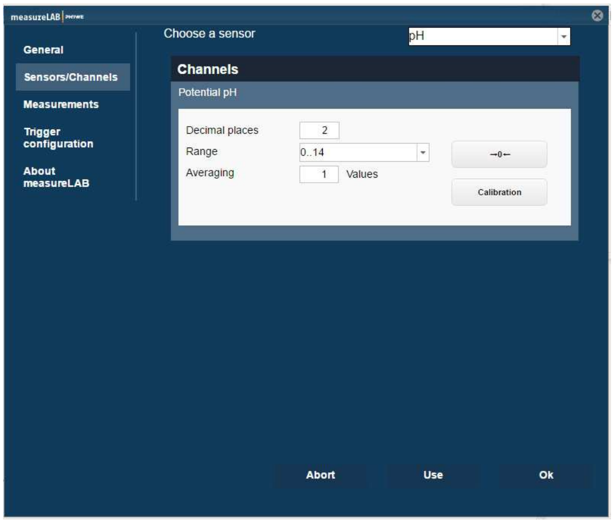

Fig. 2: pH calibration

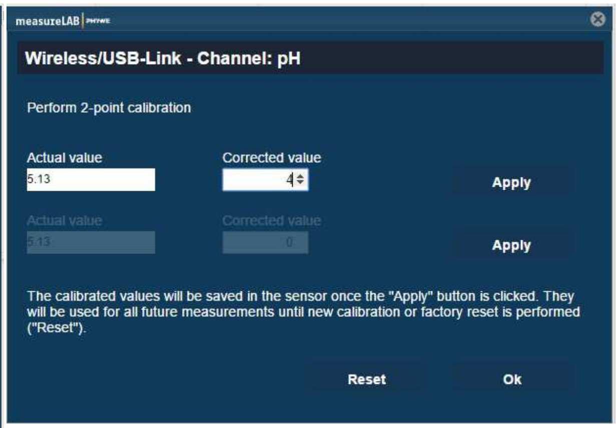

Fig. 3: pH Calibration (Correction of values)

Preparation of necessary solutions

- Prepare approximately 0.1 molar solutions of each of the carboxylic acids which are to be investigated by weighing the masses of the acids given in Table 1 into 100 ml volumetric flasks and filling them up to the mark with distilled water.

Tab.1: The masses of the carboxylic acids R-COOH to be weighed out for 0.1 molar solutions.

Acid	**R**	**Mass in g**
Formic acid	H	0.460
Acetic acid	CH_3	0.601
Monochloroacetic acid	CH_2Cl	0.945
Propionic acid	C_2H_5	0.741
Propionic acid	$CH(OH)CH_3$	1.001
n-Buytric acid	C_3H_7	0.881

Procedure

- Fill 60 ml of distilled water into a 150 ml glass beaker and add a magnetic stirring bar.
- Position the magnetic heating stirrer under the stand.
- Pipette 5 ml of the carboxylic acid solution that is to be titrated into the beaker.
- Fill the burette up to the 50 ml mark with 0.1 molar sodium hydroxide solution.
- Position the beaker containing the acidic solution on the magnetic stirrer so that the pH measuring electrode dips into the solution (*Note*: The pH electrode must dip at least so deep in the solution that the diaphragm is completely immersed in the solution. Add more water if necessary).
- Position the tap of the burette so that sodium hydroxide solution can drop into the beaker. Also ensure that individual drops will be recorded by the drop counter.
- Adjust the stirrer to a medium stirring speed (*Note:* Do not allow the magnetic stirring bar to hit against the measuring electrode.)
- Start measurement with a click on in the icon strip.
- Add sodium hydroxide solution drop-wise to the soft drink solution from the burette. (*Note*: Take care that the addition of the drops is not so rapid that the light barrier cannot register individual drops.)
- When about 10 ml of sodium hydroxide has been so added, close the tap of the burette and click on the icon to terminate the measurement.
- Save your experiment data using in the top bar.
- **Attention:** Thoroughly rinse the beaker and the measurement probes with distilled water after each titration.

Fig. 4 shows the graph for formic acid as presented by the programme. To have the equivalence point and the pK_a value displayed use .

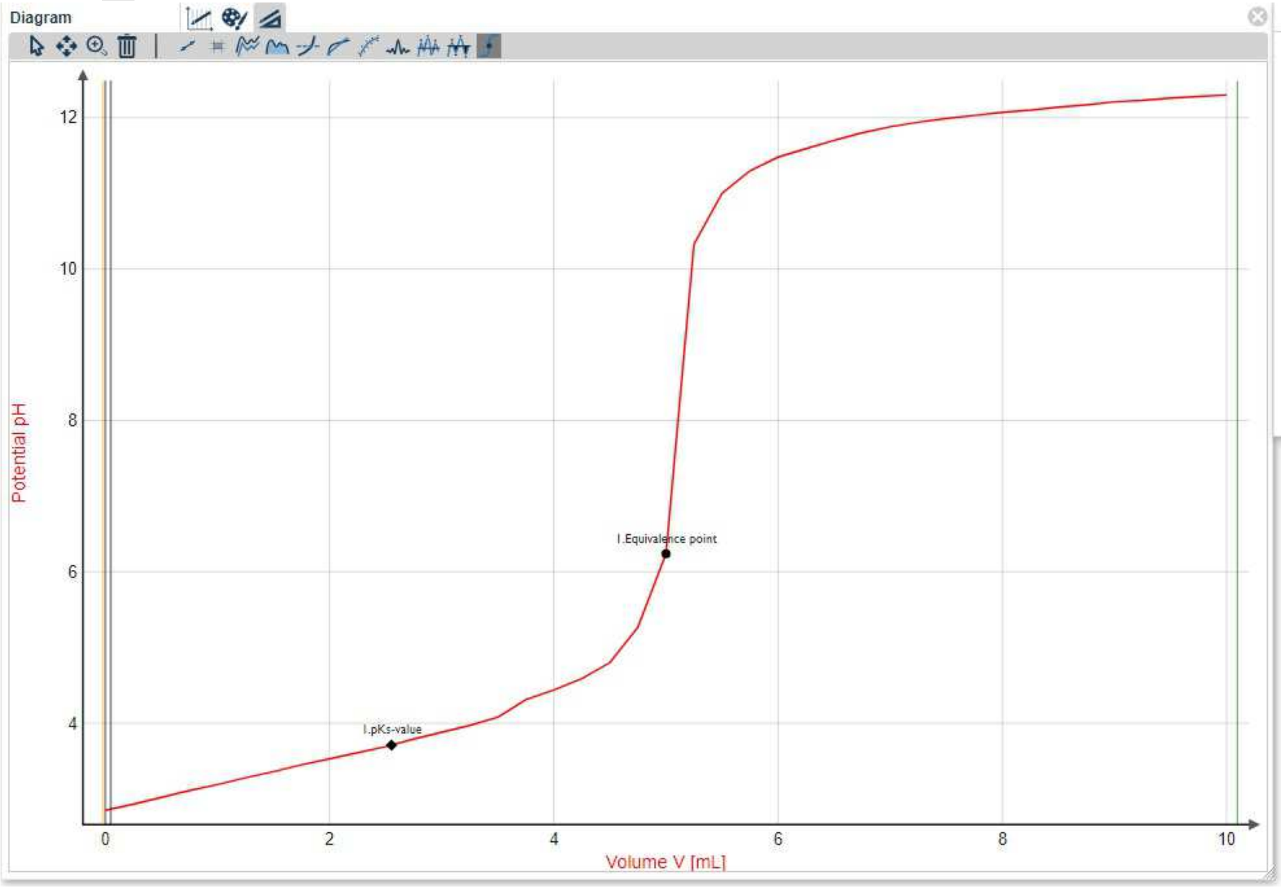

Fig. 4: Determination of the pKa value of formic acid from the neutralisation curve.

Theory and evaluation

Theory and evaluation

Carboxylic acids R-COOH are weak electrolytes, which are only partially dissociated in a aqueous solutions, i.e.

$$R-COOH \rightleftharpoons R-COO^- + H^+$$

The position of the dissociation equilibrium is quantitatively characterised by the dissociation or acid constant K_a or the pK_a value, from which it is derived.

$$K_a = \frac{\alpha_{R-COO^-} \alpha_{H^+}}{\alpha_{R-COOH}} \approx \frac{c_{R-COO^-} c_{H^+}}{c_{R-COOH}} \quad (1)$$

(α_i = activity of the substance i. In extremely diluted solutions with intermolecular or interionic interactions which can be neglected, it is equal to the concentration c_i .)

$$pK_a = -\log K_a \quad (2)$$

When the formulation (2) and the analogous definition of the pH value are taken into consideration and the logarithm is taken, the Henderson-Hasselbalch equation (3) is obtained from (1). This new equation describes the correlation between pH value and the composition (c_{R-COOH}/c_{R-COO^-}) of buffer systems or the proportion of both forms on the total concentration ($c_0 = c_{R-COOH} + c_{R-COO^-}$) of the weak acid for a given acidic strength (pK_a).

$$pK_a = pH + \log \frac{c_{R-COOH}}{c_{R-COO^-}} \quad (3)$$

During successively neutralisation of a weak acid, c_{R-COO^-} corresponds virtually to the concentration of the salt formed. In contrast, the equilibrium concentration c_{R-COOH} is identical to the remaining total acid concentration c_0 .

If half of the acid has reacted (half neutralisation), it follows that $c_{R-COOH} = c_{R-COO^-}$ and (3) becomes (3.1).

$$pK_a = pH \quad (3.1)$$

The pK_a value of a weak acid is thus equal to the pH value at half neutralisation. This can be potentiometrically determined via the measurement of the cell voltage U between a hydronium-ion-sensitive electrode (glass electrode) and a reference electrode (silver chloride electrode), which are available in combination as single-rod glass electrodes (measuring chains).

Subsequent to calibration with buffer solutions of known pH, the linear relationship between pH and U in the measuring sequence in the glass electrode:

$$U = const. \cdot pH + const.' \quad (4)$$

is saved in the Cobra4 Sensor Unit Chemistry, so that the pH values that correspond to the measured cell voltages can be immediately displayed.

On completion of the titration, the pK_a value can be directly determined from the neutralisation curve at half neutralisation by means of equation (3.1).

At constant temperature and for the same solvent, K_a and pK_a are a function of the nature of the residue (substituent) R. Consequently, compared to R = CH_3, electron-attracting substituents (acceptors) such as R = CH_2Cl lead to a facilitated dissociation of the proton via a depression of the electron density within the carboxyl group (-I-effect) and thus to an elevation of the acid constant K_a or a decrease in the pK_a value. In contrast, electron-repelling substances (donors)such as R = C_2H_7 result in a reduction of the acidic strength via a +I-effect.

The polar substituent influence can be quantified by empirically determined substituent constants σ^* which correlate in a statistically significant manner with the determined pK_a value (Fig. 5). The σ^* constants, which are interesting in this context, are given in Table 2 together with the pK values of the investigated carboxylic acids (taken from the chemical literature) for T = 298 K.

Table 2: Literature values for the pK_a values (T = 298 K) of selected carboxylic acids $R-COOH$ and their polar substituent constants.

R	pK_a	σ^*
H	3.75	0.490
CH_3	4.76	0.000
CH_2Cl	2.85	1.050
C_2H_5	4.86	-0.100
$CH(OH)CH_3$	3.86	0.450
C_3H_7	4.83	-0.115

Data and results

Fig. 4 shows the neutralisation curve for the titration of approximately 0.1 molar formic acid with 0.1 molar NaOH. A value of 3.74 is obtained for pK_a , and this agrees well with the literature value given in Table 2 for T = 298 K. the analogously determined pK_a values of the other carboxylic acids are shown as a function of their polar substituent constants in Fig. 5. The graph of this function is nearly a straight line.

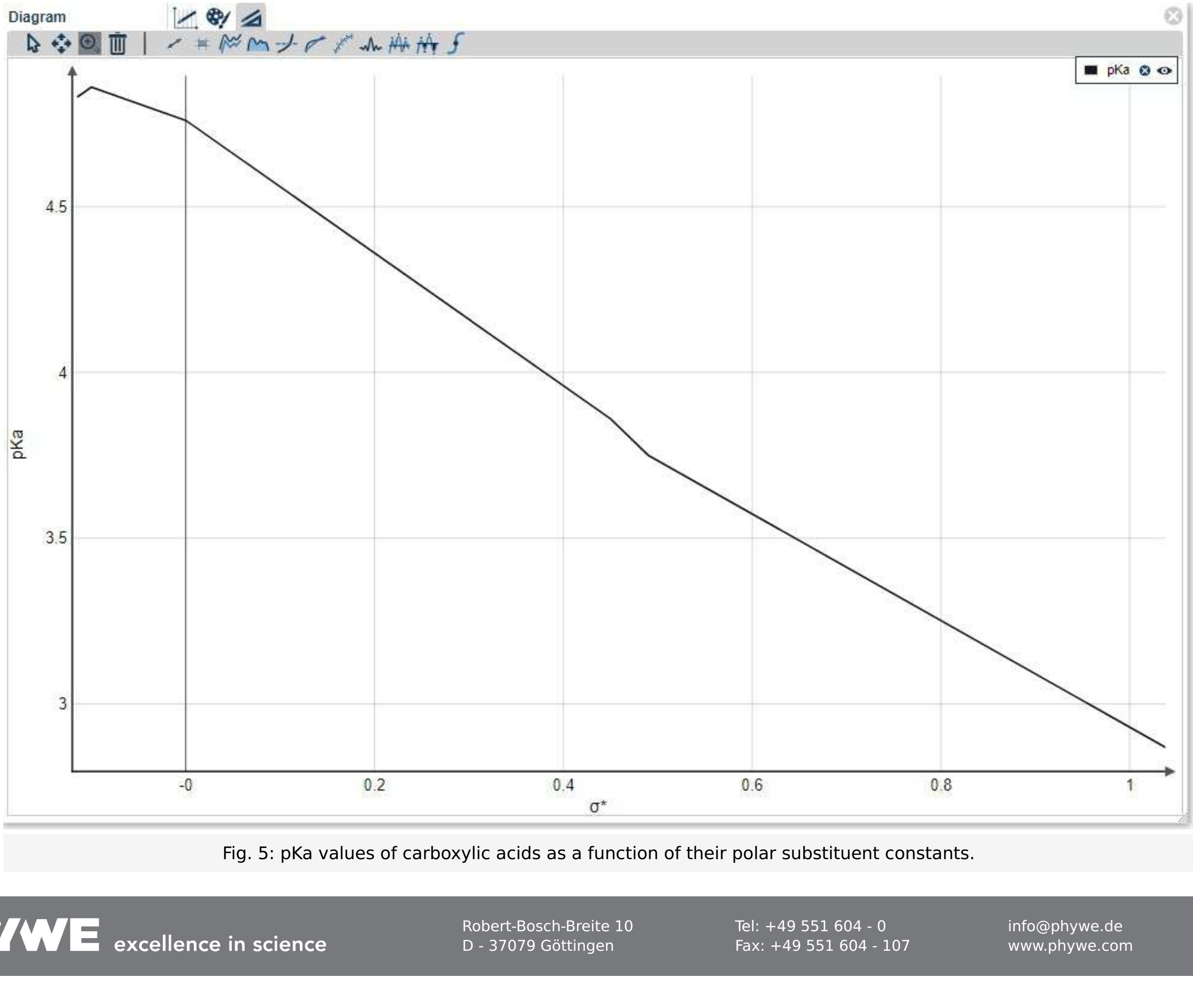

Fig. 5: pKa values of carboxylic acids as a function of their polar substituent constants.

Appendix

Disposal

The solutions which contains any monochloracetic acid or propionic acid have to be collected in a container. The diluted and neutralised solutions of the other used acids and bases can be disposed by rinsing into the drain.

Appendix

Hazard symbol, signal word	Hazard statements	Precautionary statements
Formic acid  **Danger**	H226: Flammable liquid and vapour. H314: Causes severe skin burns and eye damage.	P260: Do not breathe dust/fume/gas/mist/vapours/spray. P280: Wear protective gloves/protective clothing/eye protection/face protection. P301 + 330 + 331: IF SWALLOWED: Rinse mouth. Do NOT induce vomiting. P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing. P309: IF exposed or you feel unwell: P310: Immediately call a POISON CENTER or doctor/physician.
Acetic acid  **Danger**	H226: Flammable liquid and vapour. H314: Causes severe skin burns and eye damage.	P280: Wear protective gloves/protective clothing/eye protection/face protection. P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing. P310: Immediately call a POISON CENTER or doctor/physician.
Monochloroacetic acid  **Danger**	H331: Toxic if inhaled. H311: Toxic in contact with skin. H301: Toxic if swallowed. H314: Causes severe skin burns and eye damage. H400: Very toxic to aquatic life.	P273: Avoid release to the environment. P280: Wear protective gloves/protective clothing/eye protection/face protection. P303 + 361 +353: IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower. P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. continue rinsing. P310: Immediately call a POISON CENTER or doctor/physician. P501: Dispose of contents/container to …
Propionic acid  **Danger**	H314: Causes severe skin burns and eye damage.	P210: Keep away from heat/sparks/open flames/hot surfaces – No smoking. P241: Use explosionproof electrical/ventilating/light/…/equipment . P303 + 361 +353: IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower. P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. continue rinsing. P405: Store locked up.

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			P501: Dispose of contents/container to …
N-butyric acid  **Danger**		H314: Causes severe skin burns and eye damage.	P280: Wear protective gloves/protective clothing/eye protection/face protection. P301 + 330 + 331: IF SWALLOWED: Rinse mouth. Do NOT induce vomiting. P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. continue rinsing. P309: IF exposed or you feel unwell: P310: Immediately call a POISON CENTER or doctor/physician.
Lactic acid  **Danger**		H318: Causes serious eye damage. H315: Causes skin irritation.	P280: Wear protective gloves/protective clothing/eye protection/face protection. P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. continue rinsing. P313: Get medical advice/attention.
Caustic soda  -		H314: Causes severe skin burns and eye damage. H290: May be corrosive to metals.	P280: Wear protective gloves/protective clothing/eye protection/face protection. P301 + P330 + P331: IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.