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On Acid-Base Equilibria in Non-Aqueous Solutions

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The substances, which are included in the proton theory of acids and bases react with each other according to the well known general scheme:

$$\text{Acid} \rightleftharpoons \text{Base} + H^+$$

If they are arranged in a hydrogen bond series, starting with the one that has the greatest tendecy to give up protons, the first member of the series will act as an acid towards all the others, while the last member will act exclusively as a base. All the other members of the series possess an amphoteric character, acting as bases towards the preceding members of the series and as acids towards succeeding members. Thus water acts as a base towards all those substances that give the water lattice as a whole an excess of protons, *viz.*, the classical acids, and as an acid towards those that give the water lattice as a whole a dificit of protons, *viz.*, the classical bases. This solvent effect must be general.

If we therefore choose a substance like acetic acid as a solvent for potential acids or bases, we must have the equilibria:

$$CH_3COOH + \text{Base} \rightleftharpoons CH_3COO^- + \text{Base } H^+$$

and

$$HX + CH_3COOH \rightleftharpoons X^- + CH_3COOHH^+$$

Corresponding to the general Brönsted-Lowry scheme:

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Base}_1 + \text{Acid}_2$$

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That acetic acid can act as a base appears from the electrometric titrations of Hall and co-workers [1, 2, 3]. With acetic acid as solvent they obtained neutralization curves of bases, which are unable to form salts in aqueous solutions.

According to the theory, however, neutralization curves ought not to be limited to interaction between recognized bases and acids alone; but the »base» may be a substance that is usually termed an acid. The acidic character of the solvent must in that case lie between that of the »base» and the titrating acid.

In the present investigation dichloro acetic acid was chosen as solvent, as the equilibrium

$$2CHCl_2COOH \rightleftharpoons CHCl_2COO^- + CHCl_2COOH_2^+$$

was assumed.

As will be seen from the figure, a substance like phenol gives no typical neutralization curve in acetic acid. In dichloro acetic acid, however, an unmistakable neutralization curve is obtained.

In acetic acid the following cells were measured:

Pt	$C_6Cl_4O_2$ (sat.) $C_6C_4(OH)_2$(sat.) 0.2 *M* $C_6H_5NH_2$ in CH_3COOH LiCl	CH_3COOH LiCl	$C_6Cl_4O_2$(sat.)$_{22}$ $C_6Cl_4(OH)_2$(sat.) CH_3COOH LiCl	Pt
and				
Pt	$C_6Cl_4O_2$(sat.) $C_6Cl_4(OH)_3$(sat.) 0.2 *M* $C_6H_5NH_2$ in CH_3COOH LiCl	CH_3CCOH LiCl	$C_6Cl_4O_2$(sat.) $C_6Cl_4(OH)_2$(sat.) 0.2 *M* C_6H_5OH in CH_3COOH LiCl	Pt

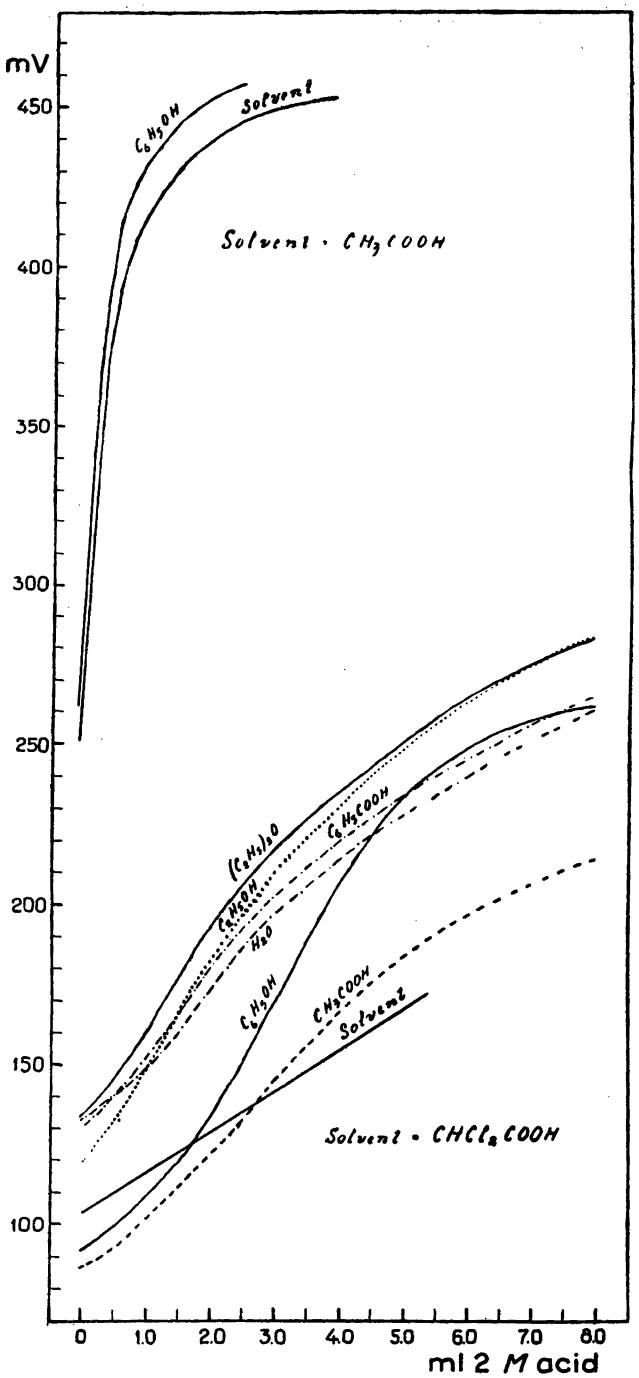
As titrating acid was used 2 *M* $HClO_4$ in CH_3COOH.

In dichloro acetic acid the cells were constituted as follows

Pt	$C_6Cl_4O_2$(sat.) $C_6Cl_4(OH)_2$(sat.) 0.2 *M* $C_6H_5NH_2$ in $CH(_3COOH$ LiCl	$CHCl_2COOH$ LiCl	$C_6Cl_4O_2$(sat.) $C_6Cl_4(OH)_2$(sat.) 0.2 *M* (X,Y.Z) in $CHCl_2COOH$ LiCl	Pt

The readings were taken at room temperature, and the titrating acid was 2 *M* H_2S_4O in $CHCl_2COOH$.

Allthough the substances which have been investigated are usually considered neutral or acid substances, the titration curves shown in the figure


mV
450
400
350
300
250
200
150
100
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ml 2 M acid
C6H5OH
Solvent
Solvent · CH3COOH
(C6H5)2O
C6H5COOH
C6H5OH
H2O
C6H5OH
CH3COOH
Solvent
Solvent · CHCl2COOH

give the typical inflections of neutralization curves. Accordingly they represent the equilibria:

$CHCl_2CCOH + C_6H_5OH \rightleftharpoons CHCl_2COO^- + C_6H_5OH_2^+$
$CHCl_2COOH + CH_3COOH \rightleftharpoons CHCl_2COO^- + CH_3COOH_2^+$
$CHCl_2COOH + C_6H_5COOH \rightleftharpoons CHCl_2COO^- + C_6H_5COOH_2^+$
$CHCl_2COOH + C_2H_5OH \rightleftharpoons CHCl_2COO^- + C_2H_5OH_2^+$
$CHCl_2COOH + (C_2H_5)_2O \rightleftharpoons CHCl_2COO^- + (C_2H_5)_2OH^+$
$CHCl_2COOH + H_2O \rightleftharpoons CHCl_2COO^- + H_2OH^+$

These results demonstrate that even »acids» may act as bases towards more acidic substances.

SUMMARY

No substance is an acid per se; but any given substance may act as an acid towards a substance with less acid strength, or it may act as a base towards a substance with greater tendency to give up protons.

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