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On Liquefaction Caused by the Trituration of Pairs of Solid Compounds

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Many pairs of solid compounds are known to give rise to liquefaction when they are brought into contact. Liquefaction is accelerated by trituration. The mode of liquefaction is of interest as an irreversible change which takes place in the contact area of two different phases. Features common to the liquefaction are twofold, *viz.*, either one or both of the solid compounds are hydrated, and the process is endothermic.[1–5]

This note deals with our search for new pairs for liquefaction and the results obtained. Since we had so far no guiding principle for selection of the pairs, we simplified the situation by choosing pairs consisting of (a) a hydrated inorganic salt and (b) an organic compound without water of crystallization (except oxalic acid). (a) is considered to supply the water necessary for liquefaction and (b) to make (a) liberate the water. Most of the salts (a) were sulfates because they are not hygroscopic but some chlorides were also tried. Chloral hydrate was taken up for the sake of comparison. For (b) we chose compounds which are able to form hydrogen bonds with water and seem to influence the structure of water. Simple amino-acids, urea,[6] acetamide which is structurally similar to urea and a series of organic acids were selected, in order to see if the change in structure might influence the mode of liquefaction.

Pairs of compounds consisting of one each from (a) and (b) were triturated in a porcelain mortar by hand for 10 min and the resulting changes were observed. Commercial products of the best grade were used. Roughly the same weights for each compound were taken. The molar ratio was made to be that of integers, *e.g.*, 5 g of $CuSO_4 \cdot 5H_2O$ and 4.8 g of urea make the ratio 1 : 4. The results are summarized in Table 1.

We see that there is no general, all-embracing rule for the occurrence of liquefaction. However, we note several interesting facts and rules. Of (a), $Na_2SO_4 \cdot 10H_2O$ undergoes liquefaction to the greatest extent, and $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ none.[7] On the other hand, $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ undergoes liquefaction very easily with several organic compounds. Of (b), polar and highly water-soluble compounds favor liquefaction, *viz.*, urea, acetamide, malonic acid, malic acid, citric acid,[8] tartaric acid and chloral hydrate. Non-polar and water-insoluble compounds have no ability to give rise to liquefaction. This is exemplified by succinic acid and fumaric acid. Isomers differ in their behavior toward liquefaction as in the cases of α-alanine and β-alanine, and maleic acid and fumaric acid.

From the results so far obtained, we might prescribe the following not rigorous but practical tests to find new pairs for liquefaction. (1) Triturate a salt from (a) with urea. If liquefaction takes place, another compound belonging to (b) which gives rise to liquefaction on being triturated with (a) can be found. If liquefaction does not take place, no (b) can be found. (2) Triturate a compound from (b) separately with $Na_2SO_4 \cdot 10H_2O$ and $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$. If liquefaction takes place, another salt belonging to (a) which gives rise to liquefaction on being triturated with (b) can be found. If not, no (a) can be found.

In certain pairs, one compound of the pair can be liquefied without being kept in contact with the other. Equivalent amounts of $Na_2SO_4 \cdot 10H_2O$ and urea, each pulverized, were put into separate branches of a bifurcated glass tube. The tube was evacuated while they were being cooled with Dry Ice and then let to stand at room temperature. Urea liquefied in less than ten days. In the case of the pair $MgSO_4 \cdot 7H_2O$ and urea, the latter did not liquefy, although the pair liquefies on trituration. In the case of $FeCl_3 \cdot 6H_2O$ and acetamide, both became wet.

Sometimes we come across pairs which on trituration give rise to chemical changes. They are exemplified by the evolution of SO_2 in the pair $Na_2S_2O_3 \cdot 5H_2O$ and citric acid, and by that of HCl in the pair $AlCl_3 \cdot 6H_2O$ and citric acid or tartaric acid, as well as by the change of color to a deep bluish violet in the pair $CuSO_4 \cdot 5H_2O$ and glycine. We realize here the necessity of giving attention to possible solid-phase reactions such as ion exchange[9] and the formation of complex compounds.

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1) Miss E. M. Walton, *Phil. Mag.*, **12**, 290 (1881).

2) T. Katsurai, *Kolloid-Z.*, **83**, 37 (1938).

3) T. Katsurai and K. Yamasaki, *ibid.*, **84**, 311 (1938).

4) T. Katsurai, *Sci. Pap. Inst. Phys. Chem. Res.* (Tokyo), **35**, 221 (1939).

5) T. Katsurai, *Bull. Inst. Phys. Chem. Res.* (Tokyo), **23**, 215 (1944).

6) D. V. Beauregard and R. E. Barrett, *J. Chem. Phys.*, **49**, 5241 (1968).

7) It is to be noticed, however, that this salt undergoes rapid liquefaction on being triturated with $FeCl_3 \cdot 6H_2O$, *cf.* (5).

8) J. W. Mullin and C. L. Leci, *Phil. Mag.*, **19**, 1075 (1969).

9) A. Clearfield and J. M. Troup, *J. Phys. Chem.*, **74**, 2578 (1970).

Table 1. Modes of liquefaction

Hydrated salt (a)	Organic compound (b) H_2NCH_2COOH glycine	$CH_3CH(NH_2)$- $COOH$ DL-α-alanine	$H_2NCH_2CH_2$- $COOH$ β-alanine	o-$NH_2C_6H_4COOH$ anthranilic acid	$CO(NH)_2$ urea	CH_3CONH_2 acetamide	$(COOH)_2$ oxalic acid, anhydrous	$(COOH)_2 \cdot 2H_2O$ oxalic acid, hydrated	$HOOCCH_2$- $COOH$ malonic acid
$Na_2SO_4 \cdot 10H_2O$	—	—	++	—	+++	++	++	+++	+++
$MgSO_4 \cdot 7H_2O$	—	—	—	—	+	—	—	—	—
$Al_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	—	—	+	—	+	—	—	—	—
$Al_2(SO_4)_3Na_2SO_4 \cdot 24H_2O$	+++	++	+++	—	+++	+++	—	+++	+
$Al_2(SO_4)_3K_2SO_4 \cdot 24H_2O$	—	—	++	—	+	—	—	—	—
$FeSO_4 \cdot 7H_2O$	—	—	+	—	++	—	—	—	—
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	—	—	—	—	—	—	—	—	—
$Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	+++	++	++	—	+++	—	++	+++	—
$CuSO_4 \cdot 5H_2O$	+	—	+	—	++	—	+	++	—
$ZnSO_4 \cdot 7H_2O$	++	—	++	—	+++	++	—	++	—
$AlCl_3 \cdot 6H_2O$	++	+	+++	—	+++	++	—	—	—
$FeCl_3 \cdot 6H_2O$	+++	+++	+++	+	+++	+++	+++	+++	—
$CCl_3CH(OH)_2$	—	—	—	—	+++	+++	—	—	—

Hydrated salt (a)	Organic compound (b) $(CH_2COOH)_2$ succinic acid	$HOOCCH_2CH(OH)$- $COOH$ malic acid	$C_3H_4(OH)(COOH)_3$ $\cdot H_2O$ citric acid	$C_2H_2(OH)_2$- $(COOH)_2$ tartaric acid	H—C—COOH ‖ H—C—COOH maleic acid	HC—COOH ‖ HOOC—CH fumaric acid	$CCl_3CH(OH)_2$ chloral hydrate	$C_6H_{12}O_6$ D-glucose
$Na_2SO_4 \cdot 10H_2O$	—	++	+++	+++	++	—	+++	++
$MgSO_4 \cdot 7H_2O$	—	—	—	—	—	—	—	—
$Al_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	—	—	—	—	—	—	—	—
$Al_2(SO_4)_3Na_2SO_4 \cdot 24H_2O$	—	—	+	++	—	—	++	—
$Al_2(SO_4)_3K_2SO_4 \cdot 24H_2O$	—	—	—	—	—	—	—	—
$FeSO_4 \cdot 7H_2O$	—	—	—	—	—	—	—	—
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	—	—	—	—	—	—	—	—
$Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	—	—	—	+	—	—	—	—
$CuSO_4 \cdot 5H_2O$	—	—	—	—	—	—	—	—
$ZnSO_4 \cdot 7H_2O$	—	—	—	+	—	—	+	—
$AlCl_3 \cdot 6H_2O$	—	—	—	—	—	—	—	—
$FeCl_3 \cdot 6H_2O$	—	—	+++	—	—	—	+	++
$CCl_3CH(OH)_2$	—	—	—	—	—	—	/	—

+++ denotes rapid and apparently complete, ++ medium, + slow and apparently partial, and — no liquefaction.