When the explosion is conducted in carbon dioxide, 0.713 milligram of tungsten gives rise to 1.01 cc. of gas which is unabsorbed in potassium hydroxide solution.

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THE ADSORPTION AND ORIENTATION OF THE MOLECULES OF DIBASIC ORGANIC ACIDS AND THEIR ETHEREAL SALTS IN LIQUID-VAPOR INTERFACES

BY H. H. KING AND R. W. WAMPLER

Introduction

It has been only within the last few years that capillarity effects have been regarded as of a chemical nature. Langmuir[1] and Harkins,[2] working independently, have developed the same theory. According to the chemical theory, surface tension is due to an attraction or residual affinity inherent to the molecule, as a result of which the molecules of the surface of a liquid are oriented in a definite manner. The structure of the surface layer is the principal factor in determining the magnitude of the surface energy. The molecules are composed of a polar group or active end and a slightly polar group, the active group being turned towards the interior of the liquid and the slightly polar group projecting up to form the surface layer. If we consider the electronic theory of matter as valid, then chemical change is due to the presence of the electromagnetic fields surrounding the atoms. Thus the surface tension is actually a measure of the potential energy due to the slightly polar groups, and accordingly the molecules will be arranged in the surface so that the stray magnetic field will be a minimum. It is readily seen that the entire molecule does not function in determining the magnitude of the surface tension, as only the slightly polar groups form the surface layer. The surface tension would also depend upon the character of the slightly polar groups and their arrangement in the surface layer.

If we should inspect the liquid hydrocarbons of the aliphatic series, we should find that they are arranged with the methyl groups forming the surface layer. This being the case we would expect the surface energy

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[1] THIS JOURNAL, 39, 1848 (1917).

[2] Ibid., 39, 354, 541 (1917).

to be practically the same for all the hydrocarbons. This is true, the surface energy ranging between 46 and 48 ergs per square centimeter. Likewise the surface layer of the alcohols is formed by methyl groups and their surface energy is practically the same as that of the hydrocarbons. The benzene molecule is assumed to lie flat in the surface due to the 3 double bonds which also have an attraction similar to that of the polar group but not of as great a magnitude. When a hydrogen atom is displaced by a polar group the benzene ring is tilted so as to stand perpendicular to the surface, this taking place in the same manner for the *ortho*, *meta* and *para* positions. If 2 adjacent hydrogens should be displaced by polar groups the surface energy does not alter much as the two cannot change the position of the benzene ring in the surface. But if the polar groups should occupy positions opposite each other as *para*, then two conditions are possible. Should the 2 polar groups be the same, or if different have the same attraction for the liquid, then the ring would assume the same position in the surface as it would if no polar groups were attached to it. The surface energy would not differ much from that of benzene. However, if the 2 groups occupying the *para* positions should be different in polar strength then the stronger would be beneath the surface while the other would be tilted slightly in the surface. The surface energy in this case would be abnormally great, due to the strong electromagnetic field about the polar groups in the surface.

When a methyl group is substituted in the ring for a hydrogen the surface energy decreases, but it can be increased by the substitution of a polar group for a hydrogen in a position adjacent to the one occupied by the methyl group. Thus the methyl group is drawn below the surface and functions no more as a determining factor in the surface energy.

Evidence supporting this view of capillarity is given by the spreading of oil films on the surface of water. A dilute solution of oil in benzene of known concentration is prepared and a definite amount placed on the water. Knowing the volume of the oil placed on the surface and the area over which it has spread, it is possible to calculate the thickness of the film as well as the cross section or diameter of the molecules. This furnishes considerable evidence that the surface is only one molecule in thickness.

It is reasonable to assume that the force which causes the spreading of the oil on the water is due to an attraction of the oil molecules for the water molecules. The entire molecule is not attracted by the water as that would mean complete solubility and not merely spreading. There must be some portion of the oil molecule that has an attraction for the water molecules, namely the polar group. Thus, in the case of palmitic acid the —COOH group has a great attraction for the water and this attraction is probably due to the residual affinity of the oxygen atom. If in the molecule of oil no polar group be present, we should expect no spread-

ing, and such is the case. The hydrocarbon oils do not spread, as the molecules have a greater attraction for one another than for the water molecules. From this is drawn the conclusion that slightly polar liquids have an attraction for each other, just as polar liquids have, and slightly polar liquids are soluble in each other but are not soluble in polar liquids. A corresponding statement can be made about the polar liquids. Thus, if we should have at the surface of water some acetic acid, this would dissolve in the water, due to the affinity of the carboxyl group for the water being greater than the corresponding affinity of the alkyl groups for each other. However, when the length of the chain increases, the number of CH_2 groups increases, and the product becomes less soluble, as the attraction of the slightly polar groups for each other exceeds that of the polar groups for water. The presence of a double bond increases the attraction and, therefore, the solubility. Likewise, the triple bond increases the attraction, but in either case the attraction is not nearly so great as that due to the polar groups.

Catalysis

The physical theory of catalysis was first proposed by Faraday[3] (1834) who considered that the reactants (gases) were absorbed by the catalyst. J. J. Thomson modified this, stating that catalysis is due to capillarity and thus is a surface phenomenon. If we take the thickness of the adsorbed layer as δ and the amount adsorbed per unit area as u, as stated by Gibbs' equation, then the concentration of the reactants in the layer is u/δ, which is the active mass of the solute. If we consider liquid solutions then the concentration of the reactants is greater at the surface of the catalyst than in the interior of the solution; consequently the velocity of the reaction is greater than it otherwise would be if the reactants were not adsorbed.

Experimental Procedure

The acids used were either recrystallized or were the purest obtainable. Oxalic acid of high purity was used after recrystallizing once from water. The succinic and fumaric acids were the purest obtainable and were used only when they checked up to the standards of the pure products. The maleic and malic acids were obtainable at the laboratory in only 10 g. amounts and were used without further purification; they were a pure imported brand. The tartaric and malonic acids were pure imported products. The esters were all prepared in the laboratory with the exception of malonic ester which was used after twice distilling, the first and last portions being discarded.

Conductivity water was used in the determination of the adsorption; its surface tension ran above 72.6 dynes at 20°. When it was possible, almost saturated solutions were made and the surface tension measured. These solutions were diluted to half of the original concentration and the

[3] Faraday-Lewis, "A System of Physical Chemistry," (second edition), vol. I, p. 457.

surface tension again measured. This was repeated until the surface tension became that of water or nearly so. The concentrations are expressed in terms of moles per 1000 g. of the solvent. The adsorption was found by the Gibbs' equation

$$u = - \frac{1}{iRT} \frac{\partial \gamma}{\partial \log C}.$$

All measurements were made at 20°. The surface-tension measurements were made with a Morgan drop-weight apparatus, the radius of the first tip being 2.7441 mm., and that of the second 2.76827 mm.

Discussion of Results

The adsorption of the dibasic acids is considerably less than that of the monobasic acids, as would be expected, and is due to the presence of the 2 strong polar groups. The attraction for water would accordingly be greater and the solubility in the surface of the liquid should be proportionately less than for the monobasic acid. The dibasic acids are, however, very irregular in their physical properties, and irregularities are to be observed in their adsorption in the surface.

Taking the first three normal acids of the series, oxalic acid is adsorbed to a very small degree while the concentration of malonic acid in the surface is much larger than that of oxalic acid. If we take solutions of 0.5 M concentration for comparison the difference in amounts adsorbed is 1.594×10^{-10} moles per sq. cm. Succinic acid is adsorbed still more than

TABLE I

OXALIC ACID $K^b = 3.8 \times 10^{-8}$

Moles per 1000 g. of water	$u \times 10^{-10}$	α	γ	Drop weight G.	Density
1.00000	0.2383	17.60	71.860	0.077980	1.0370
0.50000	0.2200	24.00	72.073	0.078290	1.0188
0.25000	0.1711	32.10	72.230	0.078526	1.0088
0.12500	0.1312	42.00	72.410	0.078755	1.0037
0.06250	....	...	72.530	0.078903	1.0009
0.03125	....	...	72.610	0.079006	0.9996
0.01562	....	...	72.690	0.079093	0.9989
0.00781	....	...	72.710	0.079125	0.9985
0.00390	....	...	72.720	0.079133	0.9983

MALONIC ACID $K = 0.158 \times 10^{-5}$

4.84520	2.8780	1.78	64.033	0.068685	1.1293
2.42260	2.4760	2.52	65.888	0.071085	1.0508
1.21130	2.4690	3.54	67.900	0.073425	1.0396
0.60565	1.8350	4.98	69.565	0.075415	1.0200
0.30282	1.2450	6.88	70.785	0.076865	1.0093
0.15141	0.8511	9.69	71.551	0.077770	1.0041
0.07570	0.4994	13.36	72.050	0.078365	1.0002
0.03785	0.2617	18.48	72.356	0.078705	0.9990
0.01897	0.0624	24.65	72.495	0.078890	0.9962

TABLE I (*Continued*)

Moles per 1000 g. of water	$u \times 10^{-10a}$	α	γ	Drop weight G.	Density
SUCCINIC ACID $K = 6.6 \times 10^{-8}$					
0.50000	2.3780	1.10	68.051	0.073703	1.0150
0.25000	1.9830	1.60	69.703	0.075630	1.0070
0.12500	1.3170	2.30	70.950	0.077080	1.0020
0.06250	0.7443	3.20	71.740	0.078006	1.0005
0.03125	0.4432	4.50	72.213	0.078540	0.9993
0.01562	0.1608	6.30	72.390	0.078720	0.9988
0.00781	0.1197	8.77	72.501	0.078880	0.9985

[a] The measurements are all made with a tip the diameter of which is 2.7441 mm. unless otherwise stated.

[b] The values of K were taken from Lehfeldt's "Electrochemistry," Part 1. General Theory, Longmans, Green and Co., 1908.

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MALIC ACID $K = 39.9 \times 10^{-8}$					
0.77360	3.7120	2.24	67.075	0.072503	1.0354
0.38680	2.1350	3.20	69.260	0.075003	1.0196
0.19340	1.4420	4.44	70.671	0.076735	1.0104
0.09670	0.9400	6.22	71.526	0.077735	1.0071
0.04830	0.4886	8.66	72.100	0.078405	1.0032
0.02394	0.3025	12.03	72.395	0.078735	1.0026
0.01146	0.1792	17.00	72.610	0.079000	1.0021
d-TARTARIC ACID[c] $K = 0.97 \times 10^{-6}$					
8.00000	−2.3810	1.09	74.125	0.079550	1.2966
4.00000	−0.7808	1.54	73.260	0.078953	1.1906
2.00000	−0.2882	2.18	72.895	0.078910	1.1110
1.00000	−0.1507	3.17	72.699	0.078840	1.0595
0.50000	....	...	72.675	0.079540	1.0345·
0.25000	....	...	72.637	0.079560	1.0184
0.12500	....	...	72.660	0.079630	1.0106
MALEIC ACID $K = 1.17 \times 10^{-5}$					
0.9352	2.1550	10.59	66.803	0.072180	1.0377
0.4676	1.9720	14.62	69.060	0.074840	1.0200
0.2338	1.2910	20.01	70.482	0.074550	1.0111
0.1169	0.8046	28.55	71.413	0.077600	1.0066
0.0584	0.4553	39.20	72.025	0.078310	1.0044
0.0292	0.2203	50.60	72.351	0.078670	1.0036
0.0146	....	...	72.556	0.078940	1.0019
FUMARIC ACID $K = 0.93 \times 10^{-6}$					
0.05000	0.4051	34.25	72.010	0.07829	1.0002
0.02500	0.2599	44.16	72.310	0.07864	0.9992
0.01250	....	...	72.506	0.07889	0.9987
0.00625	....	...	72.585	0.07893	0.9984

[c] The first four concentrations of tartaric acid were run using a tip the diameter of which was 2.7441 mm. while the rest were run with a tip the diameter of which was 2.76827 mm.

Moles per 1000 g. water	$u \times 10^{-10}$	γ	Drop weight G.	Density
	DIETHYL TARTRATE			
0.673058	6.1460	48.890	0.052035	1.0252
0.340050	5.7480	53.120	0.056780	1.0132
0.170030	5.3660	57.235	0.061410	1.0050
0.085010	4.4800	60.860	0.065545	1.0005
0.042500	4.1090	63.970	0.069095	0.9996
0.021250	3.1630	66.720	0.072245	0.9982
0.010625	2.2900	68.652	0.074465	0.9982
0.005312	1.6590	70.150	0.076185	0.9982
0.002656	1.1140	71.175	0.077375	0.9982
0.001328	0.6646	71.880	0.078170	0.9982
0.000664	0.3665	72.175	0.078515	0.9982
0.000331	0.1734	72.384	0.078750	0.9982
	DIETHYL MALONATE			
0.1344000	12.6150	43.685	0.046350	1.0008
0.0677000	8.4590	51.115	0.054570	0.9997
0.0338500	6.9470	56.705	0.060830	0.9989
0.0169200	5.4470	61.250	0.065995	0.9986
0.0084600	4.4250	64.825	0.070076	0.9984
0.0042300	3.4160	67.700	0.073365	0.9983
0.0021150	2.2760	69.750	0.075625	0.9982
0.0010570	1.2090	70.965	0.077105	0.9982
0.0005275	0.7058	71.710	0.077975	0.9982
0.0002637	0.3350	72.115	0.078435	0.9982
0.0001318	....	72.400	0.078770	0.9982
0.0000659	....	72.450	0.078826	0.9982
	DIETHYL SUCCINATE			
0.1125350	11.690	43.159	0.045740	0.9989
0.0562670	8.125	51.480	0.053690	0.9982
0.0281340	6.567	55.815	0.059835	0.9982
0.0140670	5.596	60.283	0.064895	0.9982
0.0070334	4.565	63.940	0.069060	0.9982
0.0035167	3.360	66.760	0.072290	0.9982
0.0017583[d]	2.468	68.932	0.075370	0.9982
0.0008791	1.627	70.453	0.077125	0.9982
0.0004395	0.8958	71.416	0.078230	0.9982
0.0002197	0.4664	71.870	0.078770	0.9982
0.0001098	0.3473	72.180	0.079110	0.9982
0.0000549	....	72.307	0.079175	0.9982
	DIETHYL FUMARATE			
0.0024163	4.2670	65.306	0.07118	0.9982
0.0012081	3.0210	67.970	0.07426	0.9982
0.0006040	2.0090	69.867	0.07645	0.9982
0.0003020	1.3290	71.085	0.07786	0.9982
0.0001510	0.7409	71.850	0.07874	0.9982
0.0000755	0.3554	72.215	0.07918	0.9982
0.0000377	0.1579	72.390	0.07938	0.9982
0.0000188	0.0728	72.471	0.07947	0.9982

[d] The rest of the measurements were made with a tip the diameter of which was 2.76827 mm.

malonic as would be expected but the difference is not nearly so great as that between oxalic and malonic, it being 0.594×10^{-10} moles per sq. cm. This, as before mentioned, shows a very erratic variation in the increased adsorption due to an addition of one carbon atom to the chain.

Succinic, malic and d-tartaric acids are extremely interesting when it is considered that malic and tartaric are derivatives of succinic acid. When one hydrogen of succinic acid is replaced with an hydroxyl group the surface tension is increased and a slight difference in adsorption occurs. But when two hydrogens are replaced with hydroxyls a very striking phenomenon takes place. The surface tension not only increases but becomes greater than that of the pure solvent and the concentration in the surface is less than that in the interior of the solution; that is to say tartaric acid is negatively adsorbed. If we take the structure of the carbon atom as proposed by van't Hoff and LeBel then succinic acid will be orientated so
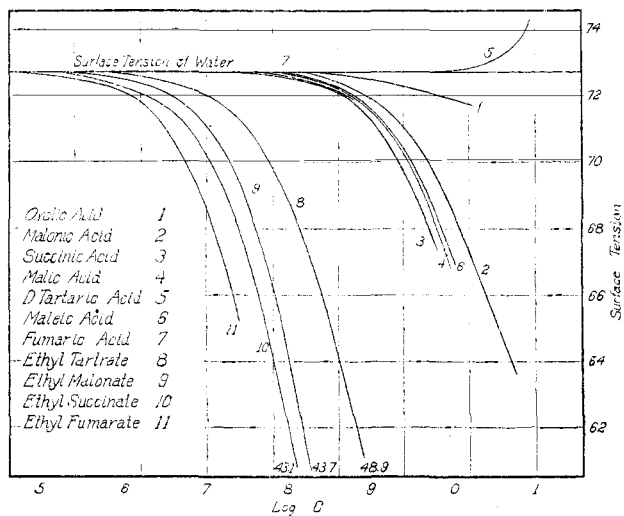
that the 4 hydrogens are in the surface and the –COOH groups in the liquid. A molecule of malic acid will be tilted in the surface, with 3 hydrogens in the surface and the 2 carboxyls and 1 hydroxyl in the liquid. Tartaric acid will have only 2 hydrogens in the surface and 4 polar groups in the liquid. The ratio of hydrogens in the surface is 4 : 3 : 2 for succinic, malic and tartaric acids, respectively, while the respective ratios of polar groups tending to draw the molecules into the solution are 2 : 3 : 4. The tartaric acid molecule is very polar as compared with succinic acid, which accounts for the negative adsorption. Also, the surface cannot be completely filled with hydrogen atoms, due to steric hindrance; consequently, there is a very strong field radiating from the polar groups which are in the liquid. The surface tension of a solution of tartaric acid is thus increased over that of the pure solvent water.

The curve for succinic acid falls a little below that for maleic acid. This is doubtless due to the double bond in maleic acid which lies very close to the surface. The two hydrogens form the surface layer, but as the carbons are larger than the hydrogens the surface cannot be packed with hydrogens. The field about the double bond thus comes into play as a factor in determining the value of the surface energy. The surface layer for succinic acid would be different in that there are 4 hydrogens in the surface per molecule of acid. The surface is thus more nearly packed than in the case of maleic acid. Also, the absence of the double bond would cause a decrease in the surface energy.

Fumaric acid is so slightly soluble that it is impossible to plot more than a short curve. This curve falls below that of malic, which in all probability is due to the divided attraction of the two carboxyl groups. The insoluble portion lies between the two groups and the double bond between the two carbons causes the molecule to be rigid and not free to rotate; thus the work which must be done by the carboxyl groups in submerging themselves is greater than that which would have to be done in the case of maleic acid. The molecule would be arranged in the surface with all atoms in the surface except the two hydroxyls in the carboxyl groups, which will be in the liquid. The area in the surface occupied by the fumaric acid molecule is considerably larger than that of maleic acid; consequently, the field intensity is less. In addition, it seems on this basis that the solubility of a "cis" acid would be greater than that of a "trans" form. Results of solubility determinations bear this out as in the case of fumaric and maleic acids and mesaconic and citraconic acids. Mesaconic acid is soluble in 38 parts of water at 14° while citraconic acid is soluble in 0.42 parts at 15°. Fumaric acid is practically insoluble, while 50 g. of maleic acid is soluble in 100 g. of water at 10°.

The diethyl esters of the dibasic acids cause a marked lowering of the surface tension. This is due to the replacement of a polar group by a strictly nonpolar group. The adsorption is greater at a much lower concentration than it is for the acids, this being due to the insoluble ethyl group. The curve for ethyl malonate lies above that of the succinate, the increase in the surface tension being due to the smaller carbon content. The molecule will be orientated in the surface layer with methyl groups forming the surface and the $=O$ in the liquid. The $-O-$ group also exerts an attraction for the liquid but this is overbalanced by the ethyl groups attached to it. The ethyl succinate will be similarly arranged in the formation of the surface. Ethyl tartrate, possessing the two $-OH$ groups, will be tilted in the surface so that the $=O$ and the $-OH$ groups will be in the body of liquid. The increase in the surface tension is due to the $-OH$ groups. Ethyl fumarate has the greatest lowering effect on the surface tension of any of the esters examined.

According to Ostwald it is only the un-ionized portion of the molecule that is effective in producing adsorption. The degree of dissociation was determined up to 50 % ionization, using the Ostwald dilution law. This factor is one that caused considerable difficulty, as the dilute solutions were calculated to be over 50% ionized. An attempt was made to determine this value by the hydrogen-ion method but it was impossible to secure checks on any of the solutions used and this method was abandoned.

Summary

1. A general explanation of the chemical theory of capillarity is given.

2. This is shown to serve as an explanation of catalysis.

3. Tables are given showing the adsorption, surface tension, drop weight and density of the different concentrations of oxalic, malonic, succinic, malic, d-tartaric, maleic and fumaric acids and for the diethyl esters of malonic, succinic, d-tartaric and fumaric acids.

4. The absorption of the dibasic acids is less than that of the monobasic acids.

5. The degree of adsorption of the dibasic acids increases with increase in carbon content; however, the increase is not regular for each carbon atom added to the chain.

6. The presence of an hydroxyl group in the molecule decreases the amount adsorbed and raises the surface tension as shown by malic and d-tartaric acids.

7. The esters are adsorbed more than the acids, due to the replacement of the polar carboxyl group by the group $-C(=O)-O-C_2H_5$.

8. The molecules are orientated in the surface with the polar groups in the liquid and the least active portions of the molecule forming the surface.

MANHATTAN, KANSAS

THERMODYNAMIC TREATMENT OF THE POSSIBLE FORMATION OF HELIUM FROM HYDROGEN

BY RICHARD C. TOLMAN

In the light of our newer knowledge concerning the structure of the atom, the suggestion has frequently been made that the nucleus of the helium atom consists of 4 hydrogen nuclei bound together by 2 electrons. If this be the case it is evident that we may write the equation 4H = He as expressing a quasi-chemical reaction.[1]

[1] Reactions for the formation of helium from hydrogen might be written in such forms as $4H^+ + 2E^- = He^{++}$; $4H^+ + 3E^- = He^+$, etc. We have chosen the particular reaction given in the text, since we shall later consider the spectroscopic evidence for the presence of un-ionized hydrogen and un-ionized helium.