calcium oxalate precipitates, which have been separated by filtration and washed with ammonium oxalate solution, can thus be transferred to a platinum dish with the aid of nitric acid before conversion to the oxide, certain defects inherent in the customary permanganate oxidation methods can be avoided.

BOSTON, MASSACHUSETTS

ADSORPTION BY SILICA FROM NON-AQUEOUS BINARY SYSTEMS OVER THE ENTIRE CONCENTRATION RANGE

BY F. E. BARTELL, G. H. SCHEFFLER AND C. K. SLOAN[1]

An interferometric method for measurement of adsorption by carbon from binary organic liquid systems was described in earlier papers from this Laboratory.[2] It was shown that, in every case investigated, the curve representing adsorption over the entire concentration range was S-shaped. The component having the higher adhesion tension against carbon was adsorbed to the greater extent. The component of lower adhesion tension was, however, preferentially adsorbed if present in sufficiently low concentration. An equation was derived which was based on the assumption that adsorption of each component of a binary liquid system follows the Freundlich equation. The equation $H \Delta x/m = a x^n (1 - x) - b(1 - x)^d x$ thus obtained was used to calculate the preferential adsorption over the concentration range.[3]

It is quite well known that carbon adsorbs better from aqueous solutions than from organic liquids, while silica adsorbs better from organic liquids.[4] Carbon has been shown to have a high adhesion tension against non-polar organic liquids and a relatively low adhesion tension against certain polar organic liquids and water;[5] the converse is true for silica.[6] From

[1] Du Pont Fellow in Chemistry, 1927–1928.

[2] Bartell and Sloan, THIS JOURNAL, 51, 1637 (1929); 51, 1643 (1929).

[3] The symbols used in this paper are the same as those of earlier papers

    H = total number of millimoles in the solution

    x = mole fraction solute at equilibrium

    Δx = mole fraction change due to adsorption

    m = weight of adsorbent

    c_0 = initial concentration

    c = final concentration

    Δc = change in concentration due to adsorption

    N = total weight (in grams) of solution

    a, n, d and b are constants

[4] Patrick and Jones, J. Phys. Chem., 29, 1 (1925).

[5] Bartell and Osterhof, Ind. Eng. Chem., 19, 1277 (1927).

[6] Bartell and Miller, ibid., 20, 738 (1928).

previous investigations in this Laboratory it has been shown that, other factors being equal, adsorption should be greatest from that liquid which has the lowest adhesion tension against a given solid adsorbent. This explains why adsorption by carbon should be greater from an aqueous solution, and why adsorption by silica should be greater from organic liquids. In the present work the interferometric method was used to determine concentration changes which occurred during the process of adsorption. Binary organic liquid systems were used with silica as the adsorbent. The results obtained are compared with those previously obtained with carbon. The experimental procedure employed was that described by Bartell and Sloan.[2]

Preparation of Silica.—The silica used was prepared by a method similar to that which had previously been used in this Laboratory.[7] A sodium silicate solution of 1.02 specific gravity was treated with concentrated hydrochloric acid in the presence of nickel nitrate. The silica gel thus formed was allowed to synerize slowly. The resulting brownish-black material was digested in conductivity water to remove nickel nitrate. This gel was then heated to 260° for two hours and again digested in conductivity water. After the nickel salt had been removed in this manner, the "silica gel" (about 15 g. per batch) was heated at 1000° for four minutes in order further to dehydrate it. At this stage the "silica" was perfectly white. It was next allowed to cool in dry nitrogen and then transferred to flasks also filled with dry nitrogen. A sufficient quantity of the "silica" was prepared to insure that uniform samples might be used throughout the course of the work.

Purification of Liquids.—Standard methods were employed for the purification of the liquids. Each liquid, after preliminary treatment, was distilled through a tall fractionating column with a large area of cooling surface. The middle fractions only were used. The liquid systems investigated were: (1) ethyl carbonate–benzene, (2) ethyl alcohol–benzene, (3) ethyl carbonate–dimethylaniline, and (4) ethyl carbonate–methyl benzoate.

Results

Adsorption from the System Ethyl Carbonate–Benzene.—The adsorption data obtained for this system when plotted give an S-shaped curve. This curve is shown in Fig. 1. Ethyl carbonate was preferentially adsorbed until a concentration of 0.68 mole fraction of it was reached. Beyond this concentration benzene was preferentially adsorbed. The values of the constants were determined by the method used by Bartell and Sloan.[2] The equation representing the adsorption over the entire concentration range for the above system is

$$H \Delta x/m = 7.603\ (x)^{0.574}\ (1-x) - 8.1798\ (1-x)^{0.982}\ (x)$$

[7] Bartell and Fu, "Colloid Symposium Monograph," Vol. VII, 1930.

The agreement between the values calculated from the equation and the values determined experimentally is shown in Table I.

TABLE I

ADSORPTION OF ETHYL CARBONATE FROM BENZENE

| c_0	m, g.	c	$\dfrac{N(c_0 - c)}{m}$	x	$\dfrac{H \Delta x}{m}$ obs.	$\dfrac{H \Delta x}{m}$ calcd.	Difference
0.0100	0.20	0.00837	0.03587	0.00556	0.31919	0.31725	−0.00194
.0500	.20	.04635	.08054	.02962	.69526	.69026	− .00500
.1000	.20	.09515	.10780	.06274	.94686	.93245	− .01441
.2000	.20	.19478	.11725	.13264	1.07050	1.06020	− .01010
.3000	.20	.29543	.10379	.20954	0.98678	0.98534	− .00144
.7483	.20	.74808	.00555	.66250	.06303	.04617	− .01691
.8883	.20	.88862	− .00804	.84062	− .09750	− .11301	+ .01551
.9500	.20	.95031	− .00747	.92359	− .09738	− .09692	− .00046
.9850	.20	.98512	− .00299	.98668	− .03925	− .03930	+ .00050
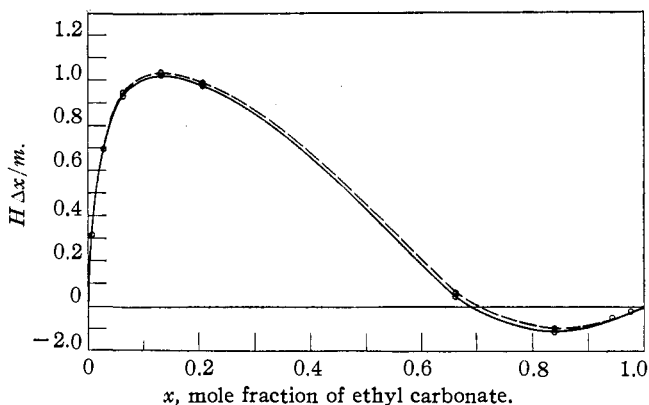
Fig. 1.—Experimental points, — — — — — —; 7.603 $(x)^{0.574}$ $(1 - x) - 8.1798 (1 - x)^{0.982} (x)$, ——————. Adsorption of ethyl carbonate from benzene.

Adsorption from the System Ethyl Alcohol–Benzene.—The results obtained with the system ethyl alcohol–benzene give an S-shaped curve, as shown in Fig. 2. Ethyl alcohol in this system is highly adsorbed at a low concentration of this component. Preferential adsorption of benzene is indicated at high alcohol concentrations.

The data obtained for the system alcohol–benzene are given in Table II. The equation representing the adsorption of this system is

$$H \Delta x/m = 8.8105 (x)^{0.227} (1 - x) - 4.664 (1 - x)^{0.615} (x)$$

For purposes of comparison, data obtained with carbon as an adsorbent[2] are plotted also in Fig. 2.

Adsorption from the System Ethyl Carbonate–Dimethylaniline.—In the system ethyl carbonate–dimethylaniline, preferential adsorption of each component is noted over some part of the concentration range.

<div align="center">TABLE II</div>

<div align="center">ADSORPTION OF ETHYL ALCOHOL FROM BENZENE</div>

c_0	m	c	$\dfrac{N(c_0-c)}{m}$	x	$\dfrac{H\,\Delta x}{m}$
0.01436	0.2622	0.00601	0.1388	0.01014	3.0108
.02745	.2503	.01720	.1783	.02882	3.8299
.04217	.2608	.03001	.1952	.04984	4.1564
.13070	.2534	.12810	.2071	.19928	4.1312
.29195	.2186	.28320	.1656	.40021	3.0001
.74883	.2540	.74810	+ .0112	.83430	0.1596
.90157	.2675	.90288	− .0200	.94035	− .2676
.96640	.2577	.96745	− .0160	.98053	− .2083
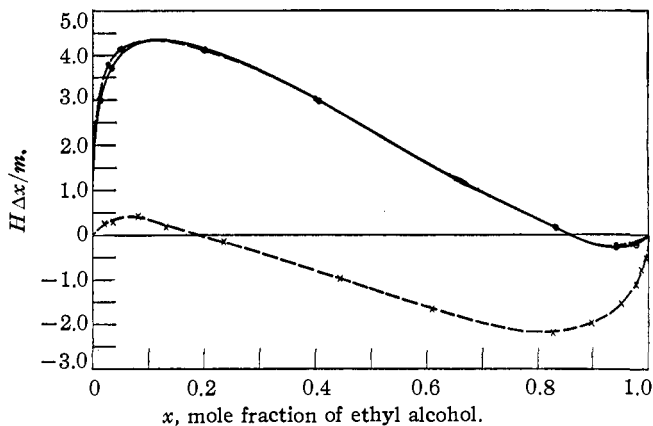
Fig. 2.—Silica (experimental), − − − −; carbon (experimental), X − − − −; $8.8105\,(x)^{0.227}\,(1-x)-4.664\,(1-x)^{0.615}\,(x)$, O − − − −. Adsorption of ethyl alcohol from benzene.

Data for this system are given in Table III, and the corresponding adsorption curve in Fig. 3. The equation representing the results obtained is

$$H\,\Delta x/m = 1.0448\,(x)^{0.658}\,(1-x) - 0.645\,(1-x)^{0.784}\,(x)$$

<div align="center">TABLE III</div>

<div align="center">ADSORPTION OF ETHYL CARBONATE FROM DIMETHYLANILINE</div>

c_0	m	c	$\dfrac{N(c_0-c)}{m}$	x	$\dfrac{H\,\Delta x}{m}$
0.01194	0.2708	0.01129	0.00835	0.01158	0.07074
.07870	.3230	.07736	.01604	.07923	.13566
.1703	.3802	.16802	.02129	.17168	.17964
.3442	.2983	.34252	.02176	.34838	.18276
.6748	.2930	.67409	.00920	.67975	.07661
.9300	.3125	.93004	.00046	.93171	− .00378
.9894	.2419	.98948	.00119	.98974	− .00985
.9958	.2581	.99585	.00067	.99600	− .00550

Adsorption from the System Ethyl Carbonate–Methyl Benzoate.—
In this system, as in the others, preferential adsorption of each of the two

components occurred over some portion of the concentration range. The adsorption curve for this system is shown in Fig. 4 and the data are given
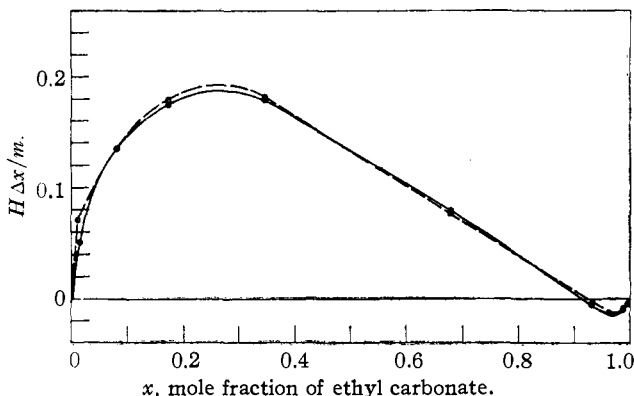

Fig. 3.—Experimental points, — — — — —; $1.0448\ (x)^{0.658}$ $(1 - x) - 0.645\ (1 - x)^{0.784}\ (x)$, —————. Adsorption of ethyl carbonate from dimethylaniline.

in Table IV. The adsorption data obtained for this system are represented by the equation

$$H\Delta x/m = 0.8479\ (x)^{0.591}\ (1 - x) - 0.1619\ (1 - x)^{0.246}\ (x)$$
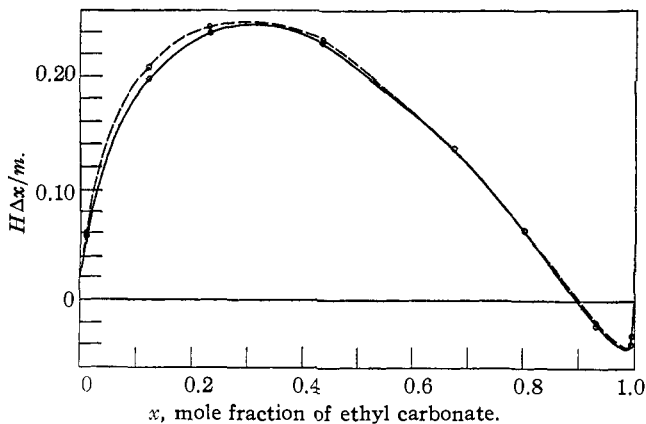

Fig. 4.—Experimental points, — — — — —; $0.8479\ (x)^{0.591}$ $(1 - x) - 0.1619\ (1 - x)^{0.2462}\ (x)$, —————. Adsorption of ethyl carbonate from methyl benzoate.

Discussion

The interferometric method had previously been used for the determination of the extent of preferential adsorption by carbon, of the components of binary non-aqueous systems over the entire range of concentration.[2] In each case investigated an S-shaped adsorption curve was obtained.

TABLE IV

ADSORPTION OF ETHYL CARBONATE FROM METHYL BENZOATE

c_0	m	c	$\dfrac{N(c_0 - c)}{m}$	x	$\dfrac{H \Delta x}{m}$
0.0106	0.2450	0.01017	0.00717	0.01172	0.06071
.1111	.2724	.10942	.02494	.12417	.20807
.2032	.2424	.20129	.03229	.23336	.27521
.4042	.2010	.40249	.03337	.43723	.26651
.6425	.3141	.64065	.02381	.67295	.13683
.7727	.2618	.77216	.00844	.79629	.06399
.9220	.2657	.92203	− .00042	.93169	− .00313
.9914	.2843	.99180	− .00520	.99516	− .03838
.9951	.2715	.99539	− .00406	.99701	− .03000

It was noted that the component having the higher adhesion tension against the carbon was preferentially adsorbed over the greater portion of the concentration range.

In the present investigation the same method was employed for the measurement of concentration changes during adsorption, but in this work silica was used as the adsorbent. It was found, as in the earlier investigation, that the component having the higher adhesion tension against the solid was preferentially adsorbed over the greater portion of the concentration range.

In general, it may be stated that the order of increasing adhesion tension values of a series of liquids against carbon is the reverse of the order of increasing values against silica. It must accordingly follow that the order of decreasing interfacial tension values of a series of liquids against carbon is the reverse of the decreasing interfacial tension values of this series of liquids against silica. One would be justified in expecting that the adsorption effects obtained with carbon would be different, in fact, practically the reverse, of the effects obtained with silica. Our results indicate that if one obtains adsorption values for a binary liquid system over the concentration range for carbon, one can by means of the adsorption curve predict with a fair degree of accuracy the degree of preferential adsorption to be expected at the different concentrations, when silica is used as adsorbent. Each adsorbent will tend to give an S-shaped adsorption curve. The one curve will tend to be the inverted and reverse form of the other. In Fig. 2 are plotted curves showing preferential adsorption values for benzene and for ethyl alcohol adsorbed with carbon and with silica. When carbon was used as the adsorbent, the non-polar liquid benzene was much more highly adsorbed than was the polar liquid alcohol; also, benzene was preferentially adsorbed over the greater portion of the concentration range.[2] With silica as adsorbent, the alcohol was more highly adsorbed than was benzene and it was also preferentially adsorbed over a greater portion of the concentration range.

Zero preferential adsorption with carbon comes at a concentration of approximately 0.2 mole fraction of alcohol, and with silica at a concentration of approximately 0.82 mole fraction of alcohol. At zero preferential adsorption both components are adsorbed, but they are adsorbed in the same proportions as represented by the concentration of the bulk of the solution.

Summary

1. In a study of the adsorption by silica from non-aqueous binary systems over the entire concentration range the interferometric method was used to measure changes in concentration of solutions.

2. In each system investigated an S-shaped adsorption curve was obtained. Over some portion of the concentration range each of the components was preferentially adsorbed.

3. The adsorption curve obtained with silica as adsorbent is very nearly the inverted and reverse form of that obtained with carbon for the same binary liquid system.

4. That component having the higher adhesion tension against the solid is preferentially adsorbed over the greater portion of the concentration range.

5. The Freundlich equation when so modified as to express the measure of adsorption in terms of change in concentration, as

$$H \Delta x / m = a x^n (1 - x) - b (1 - x)^d x$$

was found to express the adsorption as determined over the entire range of concentration.

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ADSORPTION BY SILICA AND CARBON FROM BINARY ORGANIC LIQUID MIXTURES OVER THE ENTIRE CONCENTRATION RANGE

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Several different investigators have used different adsorbates, constituting an homologous series, in their studies of adsorption with silica.[2] A variety of solvents have been used in such work, but measurements

[2] Bartell and Fu, J. Phys. Chem., **33**, 680 (1929); Holmes and McKelvey, ibid., **32**, 1522 (1928); Th. Sabolitschka, Pharm. Z., **74**, 382 (1929).