Summary

1. The use of the interferometer in measuring the change in concentration due to adsorption from non-aqueous solutions is discussed.

2. Data are given for the adsorption by carbon of α-bromonaphthalene, benzene and ethyl carbonate from dilute solutions in ethyl alcohol.

3. It is pointed out that the adsorption of these solutes by carbon tends to be in the same order as the adhesion-tension values of these same solutes (as pure liquids) against carbon. It is probable that this relationship would obtain in all cases were it not for the influence of other factors such, for example, as solubility of solute with solvent.

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ADSORPTION BY PURE CARBON FROM NON-AQUEOUS BINARY SYSTEMS OVER THE ENTIRE CONCENTRATION RANGE[1]

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Since the accuracy in measurement of change in concentration by the interferometric method is practically independent of concentration, this method was used to study adsorption from non-aqueous systems over the entire concentration range. A series of dilute solutions of ethyl alcohol in benzene was prepared and adsorption by activated carbon measured (Table I) in the manner described in an earlier paper.[3]

TABLE I

ADSORPTION OF ETHYL ALCOHOL FROM BENZENE

Init. alc. concn., $1 - c_0$	m	Δc	$1 - c$	$N\Delta c/m$	x	$H\Delta x/m$
0.01129	0.1777	0.00054	0.01075	0.0118	0.0180	0.255
.02252	.2349	.00098	.02154	.0158	.0359	.337
.04397	.1987	.00101	.04296	.0195	.0806	.412
.08137	.2575	.00067	.08070	.0099	.1294	.203
.15440	.2308	−.00048	.1549	−.0083	.2370	−.164

First, consider the adsorption of benzene when present in relatively small concentration. When the values of log $H\Delta x/m$ are plotted against log $x°$,[4]

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[1] The material presented in this paper is from a dissertation submitted by C. K. Sloan to the Graduate School of the University of Michigan, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1928. This paper was presented at a meeting of the Colloid Division of the American Chemical Society at Swampscott, September, 1928.

[2] DuPont Fellow in Chemistry, 1927–1928.

[3] Bartell and Sloan, THIS JOURNAL, **51**, 1637 (1929).

[4] The symbols used in this paper are the same as those used in an earlier paper: H = total number of millimoles in solution; x = molar concentration; Δx = change in molar concentration; m = weight of adsorbent; c_0 = initial concentration; c = final concentration; N = amount of solution; and a and n are constants.

a curve is obtained which is decidedly concave toward the concentration axis (Fig. 2). It has been shown that the Freundlich equation must be modified when the adsorption is measured in terms of change in concentration, the modified equation being, $H\Delta x/m = ax^n(1 - x)$.

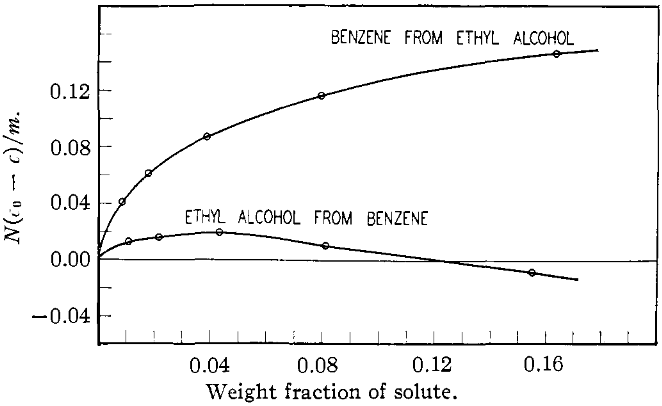

Fig. 1.—Benzene from ethyl alcohol.

The plot of the difference between log Hx/m and log $(1 - x)$ against log x should give a straight line if the adsorption of benzene follows the Freundlich equation and if no solvent is adsorbed simultaneously.

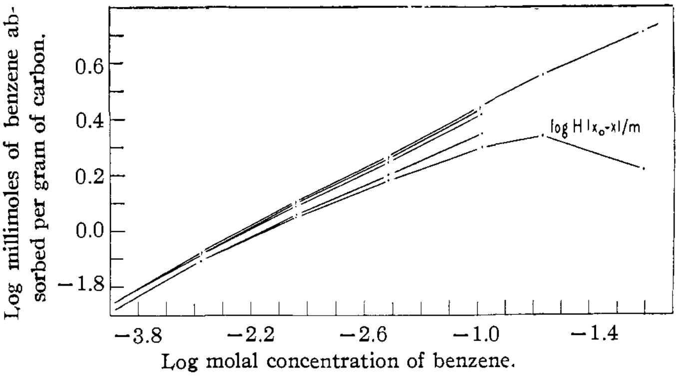

Fig. 2.—Benzene from ethyl alcohol by successive approximations.

A plot of log $H\Delta x/m$ − log $(1 - x)$ against log x gives almost a straight line, though there is still a tendency to concavity toward the concentration axis. This must be due either to a decrease in the adsorption of benzene caused by the presence of ethyl alcohol, or to the fact that simultaneous adsorption of ethyl alcohol and benzene results in a smaller change in concentration than would result if benzene alone were being removed from solution.

An insight into what occurs is obtained by considering the changes in concentration resulting when carbon is added to solutions containing small amounts of ethyl alcohol. The data show that there is an adsorption of ethyl alcohol in this range. This does not mean that benzene is not taken up by the carbon. The number of molecules of benzene adsorbed at the carbon–solution interface may still greatly exceed the number of ethyl alcohol molecules adsorbed, but the fact that a lowering of concentration of alcohol results in the bulk liquid means that a higher concentration of alcohol exists in the adsorbed layer than in the bulk liquid. This process must be classed as selective adsorption of ethyl alcohol, even though actually a greater number of benzene molecules is adsorbed. The plot of $H\,\Delta x/m$ against the concentration of alcohol $(1 - x)$ gives a curve similar to the curve for adsorption from very dilute solutions. The concavity of the log curve is more pronounced than that representing the adsorption of benzene from dilute solutions in ethyl alcohol. Thus, at about 0.2 mole fraction of ethyl alcohol ($x = 0.8$), carbon produces no change in the concentration of the solution (Fig. 3). There probably is pronounced adsorption at this point, but the apparent adsorption of each component is zero because the concentration of the adsorbed layer is here the same as that of the bulk liquid.

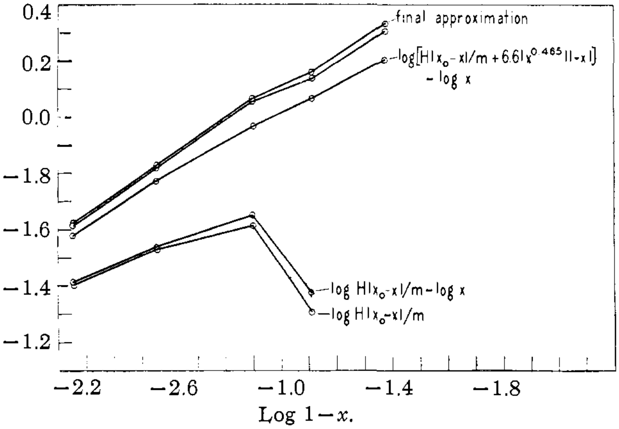

Fig. 3.—Ethyl alcohol from benzene by successive approximations.

Since the apparent adsorption of each component is in accordance with the Freundlich equation when that component is present in low concentration, it is reasonable to suppose that the Freundlich equation would be applicable for the adsorption of each component over a greater concentration range. The change in concentration due to adsorption of benzene can be represented by the following equation

$$H\Delta x_1/m = ax^n(1 - x)$$

Now let us represent the change in concentration due to adsorption of ethyl alcohol by a similar equation

$$H\Delta x_2/m = b(1 - x)^d x$$

The resultant change in concentration will be equal to the difference between these two terms. The decrease in mole fraction of benzene resulting from the simultaneous adsorption of both components is

$$H\Delta x/m = H(x_1 - x_2)/m = ax^n(1 - x) - b(1 - x)^d x$$

After this formula had been derived, it was found that such an equation had been used by Wo. Ostwald[5] to express the results of an experiment of Gustafson, who determined the adsorption from mixtures of acetic acid and phenol, concentrations being expressed in terms of weight rather than mole fraction.

Four points are necessary for the evaluation of the constants of this type of equation. The method of solution is one of successive approximations. Since the adsorption of benzene from dilute solution is governed largely by the first term of the equation, the first approximation for the constants a and n is made by plotting the difference between log $H\Delta x/m$ and log $(1 - x)$ as a function of log x. Since this plot approximates a straight line for small concentrations of benzene, two points are taken for calculation of the constants a and n, using the equation

$$\log H\Delta x/m - \log (1 - x) = \log a + n \log x$$

With this approximation the change in concentration due to adsorption can be represented by the equation

$$H\Delta x/m = 6.61x^{0.465}(1 - x)$$

This equation permits the calculation of the change in concentration due to benzene adsorption at those concentrations where ethyl alcohol is present in small amount. The measured adsorption of ethyl alcohol is then corrected by adding to it this calculated change in concentration due to benzene adsorption. The magnitude of the corrections is shown in Table II.

TABLE II

MAGNITUDE OF CORRECTIONS

EtOH concn.	$1-x$	0.0180	0.0359	0.0806	0.1294	0.2370
App. ads. of alc.	$-(H\Delta x/m)$	.255	.337	.412	0.203	−0.164
Benzene, ads.	$6.61x^{0.465}(1-x)$	.118	.234	.451	0.802	1.382
EtOH ads., corr.	......	.373	.571	.863	1.005	1.218

These corrected values are now found to be represented fairly well by the Freundlich equation. The constants b and d of the term representing the adsorption of ethyl alcohol are obtained by plotting the difference between the logarithm of the corrected value of alcohol adsorption and log x against log $(1 - x)$. This plot is much nearer a straight line than the plot obtained with uncorrected values of $H\Delta x/m$ (see Fig. 3).

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[5] Ostwald, *Kolloid-Z.*, **30**, 279 (1922); **32**, 57 (1923); **36**, 289 (1925).

The adsorption of alcohol from benzene can be represented, as a first approximation, by the equation

$$H\Delta x/m = 3.55(1 - x)^{0.550}x$$

This gives a measure of the adsorption of alcohol over all ranges of concentration. The original values for the adsorption of benzene from solutions containing small amounts of benzene can now be corrected. In this case the amount of correction is much smaller, but it does, however, tend to straighten the logarithm curve (see Fig. 2).

The difference in the successive values of the constants becomes so small after a few additional approximations that the accuracy of the experimentally determined values does not warrant further approximation. The successive series of approximations representing the change in concentration due to adsorption of each component is given in Table III. Four additional approximations result in very little change in the values of the four constants. The decrease in concentration of benzene due to adsorption from both dilute and concentrated solutions of benzene in ethyl alcohol, therefore, is obtained by combining the last two terms of the table into a single equation.

TABLE III

SUCCESSIVE SERIES OF APPROXIMATIONS

Adsorption of benzene, $ax^n(1 - x)$	Adsorption of ethyl alcohol, $b(1 - x)^dx$	Adsorption of benzene, $ax^n(1 - x)$	Adsorption of ethyl alcohol, $b(1 - x)^dx$
$6.61x^{0.465}(1-x)$	$3.55(1-x)^{0.55}x$	$8.83x^{0.514}(1-x)$	$5.69(1-x)^{0.648}x$
$8.24x^{0.508}(1-x)$	$4.89(1-x)^{0.615}x$	$9.39x^{0.526}(1-x)$	$6.31(1-x)^{0.663}x$
$8.72x^{0.512}(1-x)$	$5.19(1-x)^{0.627}x$	$9.76x_{0}{}^{.532}(1-x)$	$6.26(1-x)^{0.662}x$

$$H\Delta x/m = 9.76x^{0.532}(1 - x) - 6.26(1 - x)^{0.662}x$$

The applicability of this equation to adsorption from moderately concentrated solutions is shown by comparison with data giving adsorption of benzene at three such concentrations.

TABLE IV

ADSORPTION OF BENZENE FROM ETHYL ALCOHOL

Init. benzene concn., c_0	m	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.2690	0.1682	0.00689	0.2621	0.1548	0.1725	2.213
.5268	.2366	.00612	.5207	.1026	.3907	1.672
.6854	.2193	.00343	.6820	.0573	.5586	1.019

The agreement between experimental values and those calculated by the above equations is shown in Table V and Fig. 4.

Adsorption from the System Ethyl Carbonate-Ethyl Alcohol.—In an earlier paper[3] it was shown that ethyl carbonate is adsorbed from dilute ethyl alcohol solutions. Other measurements were made to determine the adsorption at other concentrations. The results are given in Table VI.

TABLE V

ADSORPTION OF BENZENE FROM ETHYL ALCOHOL

x	$9.76x^{0.532}(1-x)$	$6.26(1-x)^{0.662}x$	Diff.	$H\Delta x/m$	Error
0.00513	0.587	0.032	0.555	0.521	+0.034
.01050	0.855	0.065	0.790	0.787	+.003
.02289	1.280	0.141	1.139	1.123	+.016
.04854	1.857	0.294	1.563	1.537	+.026
.1033	2.616	0.602	2.014	2.022	−.008
.1725	3.173	0.953	2.220	2.213	+.007
.3907	3.608	1.761	1.847	1.672	+.175
.5586	3.160	2.034	1.126	1.019	+.107
.7630	2.004	1.841	0.163	0.164	−.001
.8706	1.174	1.406	−.232	−.203	−.029
.9194	0.756	1.097	−.341	−.412	+.071
.9641	0.344	0.667	−.323	−.337	+.014
.9820	0.174	0.430	−.256	−.255	+.001

TABLE VI

ADSORPTION OF ETHYL CARBONATE FROM ETHYL ALCOHOL

c_0	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.2781	0.00326	0.2748	0.068	0.129	0.607
.5490	.00173	.5473	.038	.321	.483
.7855	−.00033	.7858	−.007	.589	−.094
.8972	−.00118	.8984	−.030	.775	−.57
.9498	−.00075	.9507	−.020	.883	−.42
.9757	−.00038	.9761	−.010	.941	−.21

The curve representing adsorption over the entire concentration range has an S-shape (Fig. 5). Ethyl carbonate is preferentially adsorbed from solutions which are relatively dilute in ethyl carbonate; whereas ethyl alcohol is preferentially adsorbed from solutions which are relatively dilute

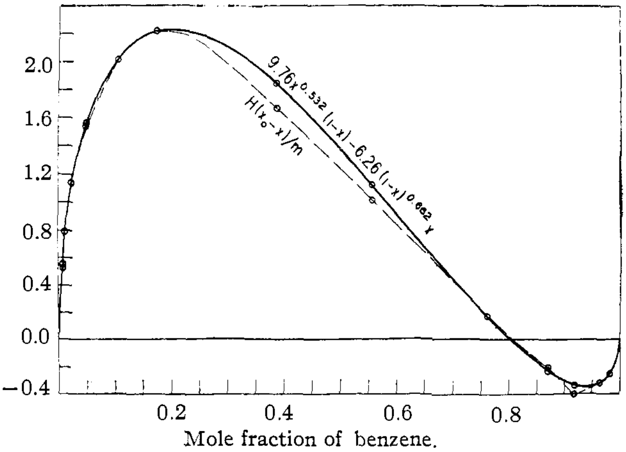

Fig. 4.—Benzene from ethyl alcohol.

in alcohol. The concave nature of the logarithm curve (see Fig. 6) shows how the change in concentration due to adsorption of ethyl carbonate is influenced by the simultaneous adsorption of solvent.

The accuracy in the determination of the change in concentration due to adsorption from this system is not so great as in the other systems investigated. This is due to the fact that there is very little difference between the refractive indices of the two components. This makes impossible an accurate calculation of the constants of the equation representing the adsorption from this system. The two parts of the S-curve are approximately the same. The exponent of the term representing the adsorption of ethyl carbonate is 0.7. The corresponding value for ethyl alcohol is 0.8.

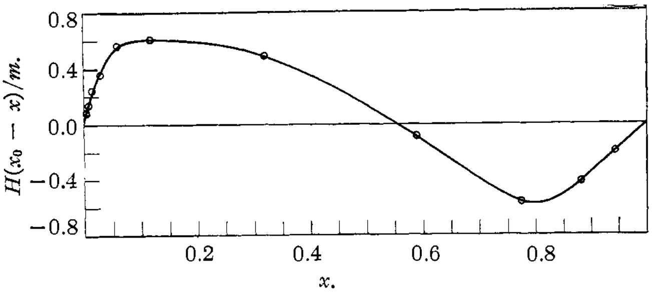

Fig. 5.—Ethyl carbonate from ethyl alcohol.

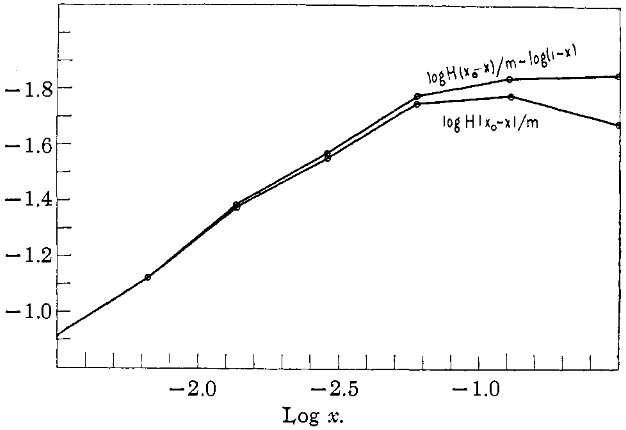

Fig. 6.—Ethyl carbonate from ethyl alcohol.

Adsorption from the System Benzene-Ethyl Carbonate.—The results of adsorption from this system are probably more striking than are those from other systems investigated. The adsorption of one of the components, benzene, conforms to the Freundlich equation up to a very high concentration of that component. This is shown by the fact that the plot

(Fig. 8) of the difference between the logarithms of $H\Delta x/m$ and x against $\log x$ is practically a straight line until x becomes 0.9. As the concentration of benzene is increased further, its adsorption is less than that indicated by the adsorption isotherm. At a molar concentration of 0.995, benzene is even slightly "*negatively adsorbed.*" This statement does not mean that benzene is not adsorbed at this concentration. There is reason to believe that the adsorption of benzene is even greater at this concentration than it is when it is *positively adsorbed* at a lower concentration. The customary use of the term, *negative adsorption*, is an unfortunate one. A reader unacquainted with the accepted meaning of this term is led to believe that the other component (ethyl carbonate in this case) makes up the adsorbed layer exclusively. It would be better to speak of this as a *preferential adsorption* of ethyl carbonate rather than a *negative adsorption* of benzene. In this system the agreement of the experimentally determined points with the Freundlich equation indicates that the adsorption of ethyl carbonate is comparatively small. The straight portion of the logarithm curve permits

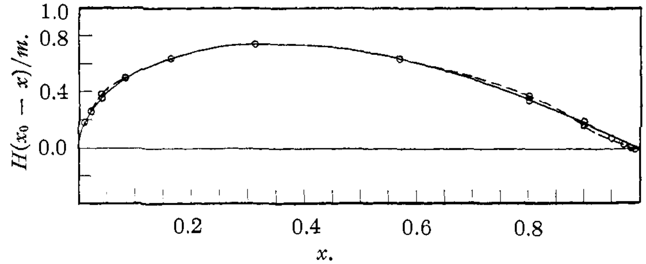

Fig. 7.—Benzene from ethyl carbonate.

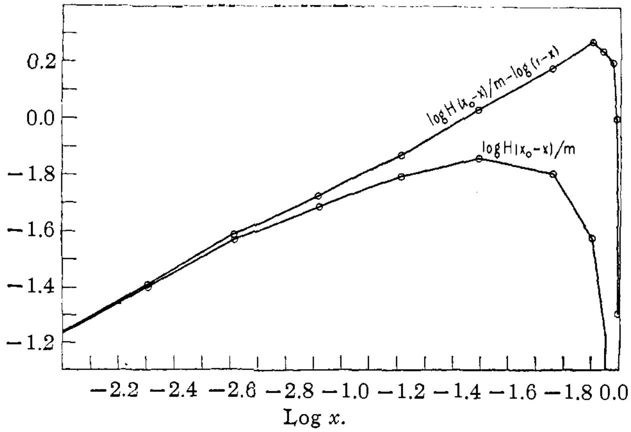

Fig. 8.—Benzene from ethyl carbonate.

a calculation of the constants of the equation representing the adsorption of benzene.

$$H\Delta x/m = 2.01x^{0.535}(1 - x)$$

The agreement between the values calculated using this equation and those experimentally determined is shown in Table VII.

TABLE VII

ADSORPTION OF BENZENE FROM ETHYL CARBONATE

c_0	m	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$	$2.01x^{0.535}(1-x)$	Diff.
0.00692	0.1788	0.00053	0.00639	0.0132	0.00961	0.165	0.165	0.000
.01414	.1839	.00053	.01336	.0195	.02006	.248	.243	−.005
.02853	.1811	.00116	.02737	.0290	.04081	.366	.348	−.018
.05808	.1846	.00155	.05653	.0391	.08306	.484	.486	+.002
.1169	.1838	.00211	.1148	.0515	.1640	.621	.638	+.017
.2330	.1917	.00281	.2302	.0649	.3113	.741	.741	.000
.4705	.3444	.00499	.4655	.0631	.5683	.642	.642	.000
.7295	.2111	.00209	.7274	.0403	.8014	.375	.354	−.021
.8590	.2061	.00096	.8580	.0185	.9013	.165	.188	+.023[a]
.93055	.2042	.00045	.93010	.0086	.9526	.075	.093	+.018[a]
.96648	.2240	.00015	.96633	.0027	.9775	.022	.045	+.023[a]
.98406	.2321	.00002	.98404	.0003	.9894	.002	.021	+.019[a]
.99243	.2072	−.00004	.99247	−.0007	.9950	−.007	+.010	+.017[a]

[a] Indicates small adsorption of ethyl carbonate.

Adsorption from the System α-Bromonaphthalene-Benzene.—The adsorption from this system is shown in Table VIII and Figs. 9 and 10.

TABLE VIII

ADSORPTION OF α-BROMONAPHTHALENE FROM BENZENE

c	0.01077	0.02401	0.04844	0.0972	0.1928	0.3570	0.6294	0.99034
$N\Delta c/m$	.0491	.0668	.0796	.0929	.0990	.0811	.0122	−.0057
x	.00409	.00919	.01883	.0390	.0826	.1732	.3903	.9748
$H\Delta x/m$	.239	.328	.396	.478	.543	.504	.097	−.022

Here, again, the adsorption curve is S-shaped. The component, α-bromonaphthalene, having the higher adhesion tension against carbon is the one which is adsorbed to the greater extent. The decrease in concentration of α-bromonaphthalene due to adsorption from this system is given fairly well by the equation

$$H\Delta x/m = 2.86x^{0.445}(1 - x) - 4.54(1 - x)^{1.05}x$$

Adsorption from the System α-Bromonaphthalene-Ethyl Carbonate.—In this system, as in others, the adsorption of the component having the higher adhesion tension is the greater. The adsorption curve has the usual characteristics.

Application of the Gibbs Equation to Adsorption at the Carbon–Solution Interface.—The results of these experiments indicate that the substance

TABLE IX

ADSORPTION OF α-BROMONAPHTHALENE FROM ETHYL CARBONATE

c_0	m	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.10015	0.0860	0.00137	0.00878	0.0774	0.00519	0.388
.02124	.1339	.00290	.01834	.1009	.01091	.508
.04404	.1025	.00262	.04142	.1185	.0249	.604
.08955	.1049	.00293	.08662	.1292	.0530	.670
.1744	.1188	.00333	.1711	.1322	.1086	.711
.3327	.1369	.00318	.3295	.1183	.2262	.687
.6006	.1068	.00112	.5995	.0607	.4695	.403
.99146	.1546	−.00008	.9916	−.0034	.9871	−.025

having the higher adhesion tension will be the one which will be adsorbed to the greater extent. No one component of a binary system, however, is preferentially adsorbed over the entire concentration range. From each of the systems investigated, the substance of lower adhesion tension is adsorbed if it be present in sufficiently low concentration in solution. This gives rise to the so-called S-shaped adsorption curve. This is in agree-

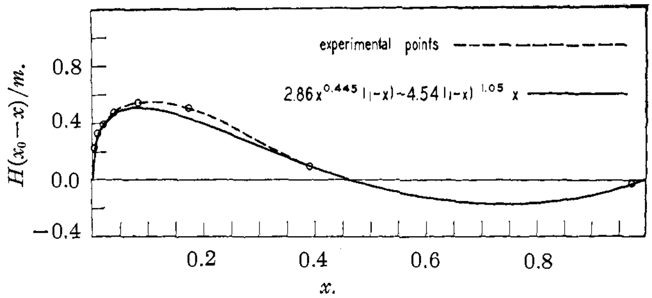

Fig. 9.—α-Bromonaphthalene from benzene.

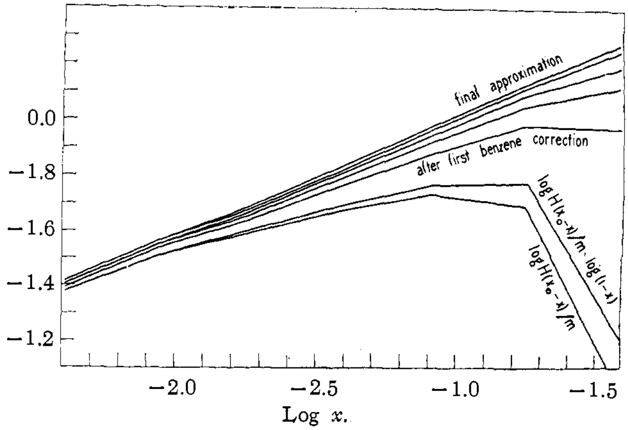

Fig. 10.—Adsorption of α-bromonaphthalene from benzene by successive approximations.

ment with the work of Williams,[6] who considered it justifiable to assume a minimum in the solid–liquid interfacial tension–concentration curve. Williams contended that the results obtained by Dora Schmidt-Walter[7] and Gustafson[8] indicating negative adsorption could be explained on the basis of the Gibbs adsorption equation[9] by considering that the addition of either component to the other which is in contact with a carbon surface will result in a lowering of the interfacial tension at the carbon–liquid interface. Although there is no method for a direct measurement of these interfacial values, the existence of such minimum points is not improbable. It has been shown that, for most binary systems, the surface tension-concentration curve does have a minimum point.[10] If the Gibbs adsorption formulation holds, the results of the experiments herein described point to a more pronounced minimum point in the interfacial tensions between a solution and carbon than between a solution and air. If the method of

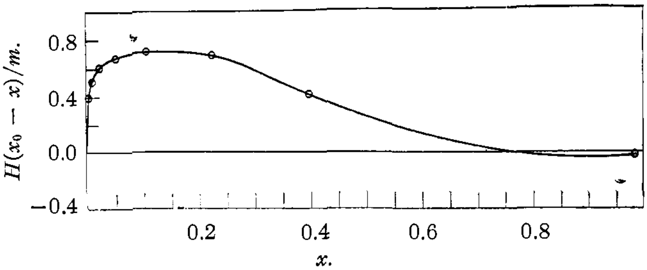

Fig. 11.—α-Bromonaphthalene from ethyl carbonate.

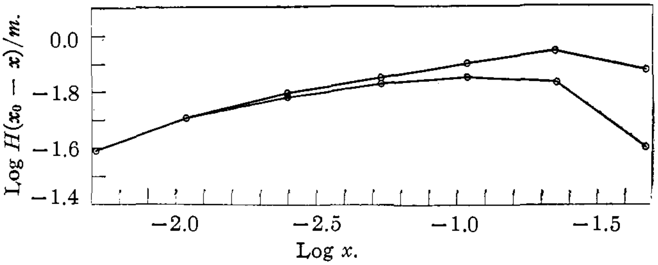

Fig. 12.—α-Bromonaphthalene from ethyl carbonate.

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[6] Williams, *Medd. Vetenskapsakad Nobelinst.*, (2) Nr. 27 (1913) (see Freundlich, "Colloid and Capillary Chemistry," p. 179); *Proc. Roy. Soc. Edinburgh*, **37**, 161 (1916); **38**, 24 (1917); **39**, 48, 52 (1918); *Proc. Roy. Soc. London*, **96A**, 287, 298 (1920).

[7] Schmidt-Walter, *Kolloid-Z.*, **14**, 242 (1914).

[8] Gustafson, *Z. physik. Chem.*, **91**, 385 (1916).

[9] Reference is here made to the rather generally used adsorption equation, $u = -(c/RT) \times dS/dc$, which has been developed from the thermodynamic rule of Gibbs relating change of concentration in the boundary layer and surface tension or interfacial tension. For lack of a better designation, this will be referred to as the Gibbs equation.

[10] Freundlich, "Colloid and Capillary Chemistry," p. 53.

Bartell and Osterhof[11] can be extended so as to measure the adhesion tension value of a binary liquid mixture against a solid, it is believed that a rigorous test can be made of the Gibbs formulation. Adhesion tension is defined by the following equation, $A_{12} = S_1 - S_{12}$. It follows that the sum of the value of the adhesion tension A_{12} and interfacial tension of a liquid against the same solid, S_{12}, must be equal to the surface tension of that solid S_1 (this latter value being constant). A change in the value of the interfacial tension with concentration at the solid–liquid interface is equal and opposite in sign to the corresponding change in adhesion tension.

$$\mathrm{d}A_{12}/\mathrm{d}c = -\mathrm{d}S_{12}/\mathrm{d}c$$

The Gibbs equation, $u = (-c/RT) \times dS_{12}/\mathrm{d}c$, then becomes

$$u = +\frac{c}{RT} \times \frac{\mathrm{d}A_{12}}{\mathrm{d}c}$$

Corresponding values of $\mathrm{d}A_{12}/\mathrm{d}c$ (adhesion measurements of solutions) and of u (interferometric measurement of change in concentration due to adsorption) should afford a test of the Gibbs formulation. Such a test has been lacking heretofore because no reliable data could be obtained for the values of both u and $\mathrm{d}S_{12}/\mathrm{d}c$ at a single interface. This correlation should establish the importance of certain factors which are disregarded by the usual formulation of the Gibbs principle. These factors include: the change of thermodynamic potential due to adsorption of solvent as well as that of solute, electrical properties of the boundary layer and the deviation of the osmotic pressure from the ideal state.

Determination of Total Adsorption.—Williams[6] realized that the measurement of the change in concentration gives only the apparent adsorption. He attempted, therefore, to obtain a second independent equation for the adsorption of each component by measuring the amount of each which is adsorbed by carbon from the vapor phase. The attainment of equilibrium in this latter procedure is not easy, as is shown by the recent work of Tryhorn and Wyatt[12] and Gustafson.[8]

Bakr and King,[13] working with a benzene-iodine-carbon system, and Bakr and McBain,[14] working with toluene and acetic acid, appear to have been successful in obtaining adsorption data for both solute and solvent for systems in equilibrium.

The fact that the change in concentration can be expressed quite accurately by a combination of two adsorption isotherms makes possible a calculation of the absolute adsorption of each component. If the equation $H\Delta x/m = ax^n(1-x) - b(1-x)^dx$ holds over the entire concentration

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[11] Bartell and Osterhof, *Z. physik. Chem.*, **130**, 715 (1927); *Ind. Eng. Chem.*, **19**, 1277 (1927).

[12] Tryhorn and Wyatt, *Trans. Faraday Soc.*, **21**, 399 (1927); **22**, 134, 139 (1927); **24**, 36 (1928).

[13] Bakr and King, *J. Chem. Soc.*, **119**, 454 (1921).

[14] Bakr and McBain, THIS JOURNAL, **46**, 2718 (1924).

range, ax^n and $b(1-x)^d$ are the respective weights of the solute and solvent adsorbed; a is the weight of solute adsorbed from pure solute. The fact that the value of a for a given solute does vary somewhat for the given solute means that the solute adsorption may be cut down to some extent by the presence of solvent. The results of Gustafson and of Bakr and McBain also indicate this. As the concentration of solute becomes large, the term $(1-x)$ decreases and the change in concentration due to solute adsorption becomes small. Even though the value of a is lower than the weight taken up from pure solute, it may still be used to represent the adsorption from the more dilute solutions.

In this investigation adsorption is expressed in terms of $H\,\Delta x/m$. In order to express the apparent adsorption more accurately, the change in concentration should be multiplied by the number of millimoles of solution after adsorption rather than the number before (H). Measurements indicate that as much as 5% of the solution may be adsorbed. The change in the value of H may therefore be quite appreciable unless relatively constant amounts of carbon and solution are used. A series of adsorption curves could be obtained over a limited range of concentration (about 50%) by using different amounts of carbon. If, for a given value of x, the value of $H\,\Delta x/m$ varies with the amount of carbon added, it will permit a calculation of the change in the value of H. This change represents the true total molecular adsorption.

Adsorption by Silica.—The measurements of Bartell and Osterhof[11] indicate that the order of the adhesion tension of different liquids against silica is opposite to the order against carbon. Thus benzene has a high adhesion tension against carbon, whereas the corresponding value against silica is low. On the other hand, the adhesion tension of ethyl carbonate is relatively low against carbon and high against silica. Since the adsorption from a binary system by carbon has been found to be dependent on the adhesion tension of the components against carbon, it is reasonable to expect that the adsorption by silica would be dependent on the corresponding adhesion tension values against silica. Thus, ethyl carbonate should be adsorbed by silica to a greater extent than benzene from solutions containing these two substances, inasmuch as the adhesion tension of the ethyl carbonate against silica is greater than that of benzene. This has been found to be the case. The results of measurements of adsorption by silica from this and other systems will be reported in a future paper. In each of the systems investigated the adsorption curve is S-shaped and the carbon and silica curves are quite opposite in nature.

Summary

The interferometric method is used to measure the adsorption by carbon from a number of binary non-aqueous systems over the entire concentration

range. In each case the adsorption curve is S-shaped. The component having the higher adhesion tension against carbon is the one which is adsorbed to the greater extent. When the component of lower adhesion tension is present in very low concentration it is, however, preferentially adsorbed.

An equation

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

is used to represent the preferential adsorption over the entire concentration range. The derivation of this equation is made on the assumption that the adsorption of each component follows the Freundlich equation.

It is pointed out that the adsorption at a given interface must depend on the rate of change of that particular interfacial tension with the concentration of the bounding phases. The importance of the measurement of adhesion tension values of solutions is pointed out since the rate of change of adhesion tension is equal and opposite in sign to the rate of change of interfacial tension with concentration.

The Gibbs principle is restated in terms of adhesion tension rather than interfacial tension. "*There will be an excess in the concentration of the solute in the interfacial layer if the rate of change of the adhesion tension of the solution against the adsorbent is positive.*" It is pointed out that the usual formulation of the principle of Gibbs does not take into consideration a number of existing factors. It is felt that a correlation of the data from adsorption and adhesion tension measurements will permit a more complete formulation of this principle.

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A MODIFICATION OF THE MOVING BOUNDARY METHOD FOR THE DETERMINATION OF TRANSFERENCE NUMBERS

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Introduction

An adaptation of the method of moving boundaries for the determination of transference numbers, involving two differences from recent procedure, has been developed and studied by the authors. The novel features are, first, a single ascending boundary only is observed and, second, a metal anode soluble under the action of the electric current is the source of indicator ions. For example, metallic silver was electrolyzed into a solution of potassium nitrate. Under the conditions of the experiment, this silver furnishes silver nitrate which serves as the indicating electrolyte for the potassium ion constituent of potassium nitrate. The necessity of previous adjustment of the concentration of the indicator electrolyte is thus avoided