[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Application of the Gibbs Adsorption Theorem to Solid–Liquid Interfaces

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The Gibbs adsorption theorem expressed in the well-known approximate form[1]

$$u = -\frac{c}{RT} \times \frac{\mathrm{d}\,S_x}{\mathrm{d}\,c}$$

has been used by many different investigators in the study of adsorption at liquid–air and liquid–liquid interfaces. Although it has been assumed that the formulation should apply to liquid–solid interfacial systems, it has heretofore not been used because no method has been available for the measurement of the interfacial tension between a solid adsorbent and solution. The recent work of Bartell and Osterhof on adhesion tension[2] has made possible the application of a modified form of the equation to solid–liquid interfaces.[3]

Numerically, adhesion tension is the difference between two quantities which are themselves quite large but not directly measurable, namely, the surface tension of a solid, S_1, and its interfacial tension against a given liquid, S_{12}; *i. e.*

$$A_{12} = S_1 - S_{12}$$

The Gibbs theorem as applied to a solid–liquid interface would be expressed as follows

$$u = -\frac{c}{RT}\frac{\mathrm{d}\,S_{12}}{\mathrm{d}\,c}$$

The measurements made by the Bartell-Osterhof method give the values for A_{12}, but not those for S_{12}. However

$$S_{12} = S_1 - A_{12}$$

Therefore

$$u = -\frac{c}{RT}\frac{\mathrm{d}(S_1 - A_{12})}{\mathrm{d}\,c}$$

and since the surface tension of the solid is independent of the concentration of the solution, we have

$$\frac{\mathrm{d}\,S_1}{\mathrm{d}\,c} = 0, \text{ and}$$

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

Accordingly, if the addition of solute tends to increase the adhesion tension of the solid–liquid system, it is to be expected that the solute will be pref-

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(1) In this equation u represents the excess concentration of the solute per sq. cm. of interface, and S_x refers to the interfacial tension at either a liquid–gas, liquid–liquid or liquid–solid interface. In this paper the different phases involved will be designated by the subscripts 1, 2 and 3, indicating solid and the different liquid phases, respectively. Thus S_2 = Surface tension liquid–gas (or air); S_{23} = Surface tension liquid–liquid; S_{12} = Surface tension solid–liquid.

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

(3) Bartell and Sloan, THIS JOURNAL, **51**, 1654 (1929).

erentially adsorbed at the interface, *i. e.*, positive adsorption demands that the term $d\,A_{12}/d\,c$ be positive.

By measuring the adhesion tensions of a series of binary solutions against silica and applying the equation developed above, the adsorption at any concentration may be calculated. Such measurements and calculations have been carried out. In the systems studied the adsorbent in each case was silica and the liquid adsorbed was ethyl carbonate. Adsorption from each of three solvents, namely, benzene, α-bromonaphthalene and dimethylaniline, was investigated. All of the liquids were first purified, then twice distilled and that fraction coming over at constant temperature was used.

It has been frequently pointed out that the behavior of organic liquids at a silica surface is very similar to that at a water surface. The data presented herein will serve to test this statement. By applying Gibbs' equation to values of the interfacial tension between the binary organic mixtures and water, it is possible to calculate the adsorption at the water interface and to compare the values obtained with those for adsorption from the same systems at the silica interface. Such calculations and comparisons have been made and are included in the tables.

Experimental

Adhesion Tension.—The adhesion tension values for the different solutions were determined by the Bartell–Osterhof[2] method, which consists in measuring the pressure of displacement of the solution by water from the minute pores formed in a tightly packed membrane of finely divided solid. From the equilibrium displacement pressure measured in the above manner, it is possible to calculate the adhesion tension of the solution against the solid by means of the equation

$$A_{12} = A_{13} - S_{23} \cos \Theta_{23}$$

A_{13}, the adhesion tension for water against a given solid is specific for that solid; values had previously been determined for water against silica. These values for water were again checked. Cos Θ_{23} was determined by the displacement pressure method mentioned above. With these data A_{12}, the adhesion tension of the second liquid system against the solid, was determined.

The solid used in this investigation was silica. It was Tripoli airfloat silica which had been treated several times with boiling 1–1 hydrochloric acid and repeatedly washed with boiling water after each treatment until no trace of acid was found in the filtrate. This treatment removed the impurities of iron and aluminum salts which were present in the original material. The final product contained less than 0.4% of impurities. All of the silica which would pass through a 350 mesh sieve was saved for this work. Before use the silica was heated in an electric muffle at about 950° for not less than two hours.

Interfacial Tension Determinations.—Measurements of the interfacial tensions of each of the solutions of the different binary systems were made by means of the double cylinder type of interfacial tension apparatus developed in this Laboratory.[4] These measurements were carried out in a small water thermostat, the temperature of which was maintained at 25 ± 0.05°.

The solutions of the different binary systems were made up accurately by weight. Concentrations are expressed in terms of mole fractions. The results obtained are given in Tables I, II and III (column 3).

The interfacial tension-concentration curves (plotted from the data) for each of the three systems were found to be smooth and regular. There was no evidence of a minimum point in any of the curves. The curves were concave upward, indicating preferential adsorption of ethyl carbonate at the water interface from each of the liquids which were used as solvents.

The adhesion tension-concentration curves were found to be similar to those expressing the interfacial tension data except that they were concave downward instead of upward. In the former case the slope d S_{23}/d c was negative, whereas d A_{12}/d c is positive. This is in agreement with the theoretical considerations discussed above. Just as in the interfacial tension-concentration curves there was no indication of any irregularity nor of a maximum point in any of the curves.

Calculation of Adsorption at Silica Interface.—If one plots the values of the adhesion tensions of ethyl carbonate solution-silica against the

TABLE I

ADHESION TENSION, ADSORPTION AND AREA OF MOLECULES

Ethyl Carbonate from Benzene[a]

Mole fraction Et_2CO_3	Density	S_{23}	Displacement pressure g./sq. cm.	A_{12} silica	Adsorption Et_2CO_3 u mole/sq. cm. At silica interface	Adsorption Et_2CO_3 u mole/sq. cm. At water interface	Area of molecules sq. cm. × 10^{16} At silica interface	Area of molecules sq. cm. × 10^{16} At water interface
0.000	0.8741	34.65	404.1	51.08	...	...	...	..
.038	.8784	31.32	350.6	55.29	1.287	0.472	15.42	22.1
.027	.8843	29.30	318.0	57.86	1.824	1.663	16.76	14.8
.113	.8880	27.60	294.9	59.73	2.207	2.115	17.42	13.3
.182	.8952	24.99	259.6	62.45	2.655	2.462	18.17[b]	16.9[b]
.301	.9080	21.99	216.1	65.87	3.025	2.817	19.09	18.0
.424	.9203	19.74	190.9	68.21	3.305	3.398	19.16	17.4
.506	.9278	18.42	172.6	69.29	3.491	3.826	19.06	17.0
.686	.9444	16.01	144.0	71.53	3.672	4.165	19.07	17.1
.864	.9590	13.92	124.3	73.08	3.814	4.600	19.00	17.1
.929	.9641	13.16	115.5	73.77	3.814	4.600	19.09	17.5
.985	.9683	12.71	110.5	74.16	3.814	4.600	19.16	17.5
1.000	.9691	12.61	109.4	74.25	3.814	4.600	19.09	17.5
						Average	19.0	17.3

[a] Radius of silica membrane pore = 1.602 × 10^{-4} cm. A_{13}, water against silica = 82.85 dynes/cm. [b] Values below b in each case were used in obtaining averages.

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[4] Bartell and Miller, THIS JOURNAL, **50**, 1961 (1928).

TABLE II

ADHESION TENSION, ADSORPTION AND AREA OF MOLECULES

Ethyl Carbonate from α-Bromonaphthalene

Mole fraction Et_2CO_3	Density	S_{23}	Displacement pressure g./sq. cm.	A_{12} silica	Adsorption Et_2CO_3 *u* mole/sq. cm.		Area of molecules sq. cm. × 10^{16}	
					At silica interface	At water interface	At silica interface	At water interface
0.000	1.497	41.84	512.3	42.60	...	...	..	..
.014	1.491	38.55	467.5	46.11	0.549	0.872	23.3	16.7
.052	1.473	34.51	407.7	50.81	2.502	1.800	14.2	17.2
.101	1.449	30.85	352.0	55.19	3.107	2.510	16.2	17.8
.236	1.383	24.84	259.6	62.45	3.107	3.220	21.6[a]	19.4[a]
.357	1.320	21.49	212.0	66.19	3.107	3.220	22.9	20.8
.490	1.253	18.86	182.1	68.54	3.107	3.220	22.7	21.3
.759	1.108	14.99	141.3	71.75	3.107	3.220	21.6	21.2
.906	1.025	13.44	122.3	73.24	3.107	3.220	21.1	20.9
.952	0.998	13.01	115.5	73.77	3.107	3.220	21.0	20.7
.976	.984	12.79	112.8	73.99	3.107	3.220	21.0	20.6
1.000	.969	12.61	109.4	74.25	3.107	3.220	20.8	20.6
						Average	21.6	20.7

[a] Values below *a* in each series were used in obtaining averages.

TABLE III

ADHESION TENSION, ADSORPTION AND AREA OF MOLECULES

Ethyl Carbonate from Dimethylaniline

Mole fraction Et_2CO_3	Density	S_{23}	Displacement pressure g./sq. cm.	A_{12} silica	Adsorption Et_2CO_3 *u* mole/sq. cm.		Area of molecules sq. cm. × 10^{16}	
					At silica interface	At water interface	At silica interface	At water interface
0.000	0.9519	25.81	224.2	65.32	...	...	..	..
.026	.9524	24.56	213.4	66.08	0.121	0.355	25.4	20.6
.052	.9529	23.78	208.0	66.51	.383	.492	22.3	22.2
.105	.9539	22.56	197.0	67.37	.638	.896	22.6	20.6
.208	.9558	20.50	179.4	68.75	.940	1.332	24.7	22.1
.311	.9575	19.01	165.8	69.82	1.174	1.606	25.1	22.4
.413	.9595	17.81	154.9	70.68	1.594	1.913	24.0	21.8
.515	.9613	16.69	144.1	71.53	1.594	2.236	24.7	21.5
.759	.9654	14.44	125.0	73.03	1.594	2.397	25.7	22.2
1.000	.9691	12.57	109.4	74.25	1.594	2.518	25.8	22.5
						Average	24.5	21.7

logarithm of the concentration of ethyl carbonate (in moles per cc.), a curve is obtained, for each solvent, which straightens out and approaches a constant slope as the concentration of ethyl carbonate increases. Since the adsorption of solute at any concentration is, according to the theorem, directly proportional to the slope of the curve at that point, it appears that "saturation" of the surface by adsorption must have been reached when this slope no longer changes. That is, from this point on the concentration of solute in the interfacial layer is in excess of the bulk concentration by a constant amount.

The calculated values for adsorption of ethyl carbonate by silica from each of the three solvents are given in the tables (column 6). It is seen that at a silica surface ethyl carbonate is adsorbed from benzene to a somewhat greater extent than from alpha bromonaphthalene, while from dimethylaniline the adsorption is much less.

The values for adsorption of ethyl carbonate at a water interface from the same three solvents are also given in the tables (column 7). The adsorption values shown in this table were calculated by applying Gibbs' equation to interfacial tension concentration data. As in the case when silica was the adsorbent, adsorption is greatest from benzene and least from dimethylaniline—an observation which is in agreement with the widely accepted view that silica and water surfaces behave very similarly toward organic liquids.

Calculation of Area of Adsorbed Molecules.—It is of interest also to compare the calculated area of molecules adsorbed at a silica surface with the calculated area of the same molecules adsorbed at a water surface. Such results are summarized in the tables (columns 8 and 9). The method of calculation is one used by Bartell and Mack[5] which has been designated the "modified mixture law" method. It is assumed that if there were no adsorption the adhesion tension–concentration curve would be a straight line. To determine the concentration of solute in the interface corresponding to any given concentration in the bulk of the solution one needs simply to draw a horizontal line from the adhesion tension–concentration curve to the straight line joining the two ends of the curve. The concentration corresponding to the intersection of the two lines is the concentration of solute in the interfacial layer. This gives the value called "total" moles per cc. in the surface. The adsorption as shown in the previous tables is the *excess* moles per sq. cm. in the surface. The total moles per sq. cm. is obtained by adding to this quantity the value of $c^{2/3}/N^{1/3}$ in which c is the concentration (moles per cc.) in the solution and N is Avogadro's number. The term $(c^{2/3}/N^{1/3})$ is moles per sq. cm. in the bulk of the solution and when added to the excess moles per sq. cm. in the surface (adsorption) gives the total moles per sq. cm. in the surface. The thickness of the surface layer, then, is given by the quotient

$$t = \frac{\text{total moles/sq. cm.}}{\text{total moles/cc.}}$$

and the area of an adsorbed molecule by

$$a = \frac{M}{Ndt}$$

where d is the density and M the molecular weight.

Bartell and Mack showed empirically that for applying the mixture law method to calculations of this sort, it was more suitable to use volume fraction than mole fraction values in expressing solution concentrations.

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(5) Bartell and Mack, *J. Phys. Chem.*, **36**, 65 (1932).

Consequently in obtaining the area values given in the tables mole fractions were converted to volume fractions and graphs were drawn from which the interfacial concentrations were determined.

The area of the ethyl carbonate molecule adsorbed on silica was found to be practically the same from the three different solvents, which indicates that the adsorption calculated by means of Gibbs' equation and adhesion tension data must be approximately correct. By an exactly analogous method the area of the ethyl carbonate molecule adsorbed at the water interface was calculated. (Column 9 in tables.) It had been previously demonstrated[5] that this method gives reliable values for the area of molecules adsorbed at liquid–liquid interfaces. The close agreement between the calculated area at the water interface and the calculated area at the silica interface is further evidence that the calculation of adsorption at solid surfaces from adhesion tension data is justified.

Summary

1. A method was developed for calculating adsorption at solid–liquid interfaces by means of the Gibbs adsorption theorem using adhesion tension data instead of surface tension or interfacial tension data.

2. Adhesion tension values against silica and interfacial tension values against water were determined for three binary liquid systems throughout the entire concentration range.

3. The order of "maximum" adsorption of a given solute from a series of three organic liquids was found to be the same whether silica or water was used as adsorbent. This is in agreement with previous observations concerning the similarity between a water surface and silica surface in their relation to organic liquids.

4. From the adsorption data and by means of the "modified" mixture law method the area of adsorbed ethyl carbonate molecules was calculated. Six values were obtained using three solvents and two adsorbents. The agreement of the values is remarkably good, justifying in large measure the use of adhesion tension data for calculating adsorption at the solid–liquid interface.

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