age deviations of Table V for the five possible mechanisms to be slightly greater than the smoothing deviations of Table II.

Summary

Using a dynamic system, the fraction of atomic hydrogen has been measured as a function of distance along the recombination tube for seven pumping speeds at pressures ranging from 0.276 to 1.044 mm. The measured fraction of atomic hydrogen varied from 0.0410 to 0.693.

The experimental data have been fitted to a family of empirical curves by the method of least squares. The resulting smoothed variables as well as calculated derivatives have been used to solve for rate constants in rigorous equations applicable to a dynamic system.

Ten mechanisms involving recombination by triple collisions have been postulated and appropriate rate constants calculated using all the smoothed experimental data to obtain unique numerical values for the rate constants in each mechanism.

On the basis of the ability of the calculated rate constants to reproduce the smoothed experimental values for the fraction of atomic hydrogen, five of the postulated mechanisms have been eliminated.

It has been pointed out that, on the basis of reproducibility, it is not possible to advocate any specific one of the remaining five acceptable mechanisms but that future definite information regarding the presence and nature of a wall reaction could determine which one of the five possible sets of rate constants should be used to describe the recombination of hydrogen atoms.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FRESNO STATE COLLEGE]

Electrical Factors in the Adsorption of Polar Molecules at the Surface of Solutions

BY ROBERT DUBOIS AND ERIC E. TODD

In an earlier paper McBain and DuBois[1] reported extensive measurements of adsorption at the air–solution interface which were made as experimental tests of the Gibbs adsorption equation

$$\Gamma_{2(1)} = -\frac{d\sigma}{RT\, d\ln a_2} = -\frac{d\sigma}{RT\, d\ln c_2} \qquad (1)$$

where $\Gamma_{2(1)}$ is the absolute excess of solute (component 2) adsorbed in 1 sq. cm. of the surface of a binary solution, σ is the surface tension of the solution, and a_2, c_2 are, respectively, the activity and the molar concentration of the solute in the bulk solution. ($\Gamma_{2(1)}$ is defined in the Gibbs manner[2] so that $\Gamma_1 = 0$.) The adsorption of various solutes on the surfaces of moving bubbles was measured and found to be much larger than the values calculated by means of the above equation. These results confirmed the earlier measurements of McBain and Davies[3] made with similar apparatus and are in line with the excessive adsorption found by other workers using dynamic methods of measurement.

As a result of this apparent failure of the Gibbs equation to account for the experimental values, it has been suggested by several writers that an electrical term should be added to the equation to take account of the known electrification of the bubbles and drops upon which the adsorption takes place. The validity of such suggestions will be discussed later; their implication is that the excess of the observed adsorption over the calculated value is of electrical origin. As part of a general investigation of the factors responsible for the excessive adsorption on moving bubbles, the present authors have undertaken to test the electrical explanation by measuring the effect of enhanced electrification of the bubbles on the observed adsorption.

Meaning of the Term "Electrification."—The term "electrification of bubbles and drops" may refer to any of the following:

(1) *Electrokinetic double layer*, the electrical double layer which always exists at the surface of any bubble or drop in contact with water or an aqueous solution and whose parts may be tangentially displaced under the influence of an external electric field. The charge which is thus made evident by cataphoretic migration originates in the dissociation of a surface layer, either a part of the

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[1] McBain and DuBois, THIS JOURNAL, 51, 3534 (1929).

[2] Gibbs, "Collected Works," Longmans, Green and Co., New York, N. Y., 1928, Vol. I, p. 234.

[3] McBain and Davies, THIS JOURNAL, 49, 2230 (1927).

primitive particle (*e. g.*, oleic acid droplets in water) or adsorbed thereon (adsorption of sodium oleate on oil drops, fatty acids on air bubbles).

(2) *Oriented dipole layer*, composed of adsorbed polar molecules arranged with more or less complete vertical orientation in the surface. Changes in the number and orientation of these adsorbed molecules are evidenced by changes in surface tension and by variations in the interfacial potential first observed by Kenrick[4] and later more extensively studied by Frumkin,[5] and others. The distinction between the "electrokinetic" and the "oriented dipole" double layers has been discussed recently by Chalmers and Pasquill.[6] The elements of the latter kind of double layer are of course fixed in the molecules themselves and are not displaceable in an external electrical field.

(3) *Space charge in the interior of a gas bubble.* It has been known for many years that a gas may become electrically charged by having liquid sprayed into it or by bubbling it through a liquid. For example, Lord Kelvin[7] bubbled air, hydrogen, and other gases through water and aqueous solutions of various (organic and inorganic) substances and found that in all cases the gas became electrically charged. Similar observations were made by Coehn and Mozer[8] with solutions of organic compounds.

The first two of these electrical states cannot be altered by the experimenter except by changing the concentration of the solute or by the addition of other solutes whose adsorption would necessitate additional terms in the adsorption equation. Moreover, any electrical contribution to the surface energy which is due to adsorption of the solute and whose magnitude is determined by the bulk concentration of the solution, is implicitly included in the Gibbsian equations. This may be seen if we write equation (1) in the more general form

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \qquad (2)$$

or

$$\Gamma_{2(1)} = -d\sigma/d\mu_2 \qquad (3)$$

and note that μ_2, the chemical potential of component 2 (the solute), is definable by the equation

$$\mu_2 = \left(\frac{\partial E}{\partial n_2}\right)_{S,V,n} \qquad (4)$$

Here E, the total energy of the system, represents the sum of the energies of all portions thereof, including the surface layer, and includes every kind of energy possessed by any part of the system. (S, V, n represent constancy of the variables entropy, volume and number of moles of all components other than 2.)

The third electrical condition, space charge in the gas, can be varied without changing the composition of the solution, and we planned, therefore, to investigate the effect on the adsorption of organic molecules on the surface of moving bubbles which might be brought about by alterations in the electrification of the gas.

Experimental

The apparatus and method of measurement used in this work were practically identical with those employed by McBain and DuBois and have been described in detail in their paper.[1] The electrical bubble counter there mentioned was modified by replacing the vacuum tube circuits with a photoelectric cell and suitable relays actuated by the passage of the bubbles through a beam of light. All the experiments to be described were made with solutions of *p*-toluidine in boiled-out distilled water at a fixed concentration of 2.0 g. of *p*-toluidine per kg. of water. The toluidine was the best obtainable from Kahlbaum and was further purified by sublimation after mixing with solid potassium hydroxide. The "Gibbs value" for the adsorption of *p*-toluidine at the concentration given is 7.1×10^{-8} g./sq. cm. (ref. 1, page 3546). The experimental values obtained from measurements with moving bubbles are generally about twice this value.

Effect of Discharging Gas.—We were interested first in determining whether any charge could be detected in the gas escaping from the collapsed bubbles. For this purpose we interposed in the gas stream at the outlet of the adsorption tube a Kelvin electric filter.[9] This was made by packing clean brass filings in a 6-in. (15-cm.) length of $^1/_2$-in. (1.27-cm.) tin pipe and supporting this pipe inside a metal shield tube by means of insulated glass tubes set in brass end caps. The filter was connected to the ungrounded side of a 1 mfd. condenser. While a stream of gas bubbles was passing through the apparatus, the condenser was allowed to accumulate charge for various periods of time (up to ten minutes) and was then shorted to ground through a sensitive galvanometer. Although no evidence of charge was observed with the ordinary rate of bubbling, unusually vigorous bubbling caused a small galvanometer deflection. Evidently a small charge must have been present in the ordinary gas stream. Now the nitrogen gas used to create bubbles in the adsorption tube passes first through two long saturators filled with the same solution and must already possess a charge when it reaches the adsorption tube. We decided, therefore, to discharge the gas just before entering the bubbling nozzle and observe the effect, if any, on the measured adsorption.

A three-way stopcock was placed in the gas line just before the adsorption tube so that the nitrogen could either

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(4) Kenrick, *Z. physik. Chem.*, **19**, 625 (1896).

(5) Frumkin, *ibid.*, **111**, 190 (1924).

(6) Chalmers and Pasquill, *Phil. Mag.*, [7] **23**, 88 (1937).

(7) Kelvin, Maclean and Galt, *Proc. Roy. Soc.* (London), **A67**, 335 (1895).

(8) Coehn and Mozer, *Ann. Physik*, [4] **43**, 1048 (1914).

(9) Kelvin, Maclean and Galt, *Proc. Roy. Soc.* (London), **A61**, 483 (1897); *Trans. Roy. Soc.* (London), **A191**, 187 (1898).

be passed through a grounded Kelvin filter interposed at this point or allowed to by-pass the filter and enter the tube directly. A number of adsorption measurements were made in succession, both with and without discharging the gas, and without any other change in the experimental conditions. No variation in the adsorption values could be observed other than those usually found in duplicate determinations.

In the face of the negative results on discharging the gas, we decided to enhance the electrical effect, if there was one, by forced charging of the gas stream before it entered the adsorption tube.

Spark Discharge.—We first tried the effect of a spark discharge between platinum wires sealed into the inlet to the adsorption tube. Several experiments were conducted in the usual manner until constant results were obtained. Connection was then made to an induction coil without disturbing the bubble rate or the overflow rate. A marked change immediately became apparent in the adsorption tube. The bubbles, which had previously maintained a steady stream, began to bunch and coalesce. As shown by the interferometer readings, the adsorption appeared to drop considerably, and with succeeding experiments even became negative. However, when the sparking was interrupted and additional adsorption measurements were made, the effect was found to persist, since the adsorption values rose only very slowly and the bubbles continued to bunch. Because of its persistence after sparking ceased we concluded that the effect observed was not electrical but was due to the chemical action of some product or products formed in the discharge.

Ionization by Alpha Particles.—In order to avoid the chemical effects caused by electrical discharge we produced ionization in the nitrogen gas by means of alpha particles. A few milligrams of ionium bromide was placed on the bottom of a small flask interposed in the gas line between the last saturator and the adsorption tube. Since about 0.4 cc. of nitrogen gas per second passed directly over several milligrams of ionium emitting 8×10^6 alpha particles per mg. per sec., each capable of producing 1.4×10^5 ions in a range of 2.85 cm., it is evident that an enormous number of ions would be present in the gas as it passed on to the bubbling nozzle. Preliminary tests with a Kelvin filter placed between the ionization chamber and the nozzle demonstrated that a charge did exist in the gas stream. No evidence of charge could be detected in the gas leaving the adsorption tube, indicating, as would be expected, that the initial charge had disappeared because of ion recombination and adsorption on the bubble surfaces during the twelve seconds required for the bubbles to pass along the 156 cm. tube.

In order to test the effect of the ionization of the gas on the adsorption of *p*-toluidine on the bubble surfaces, a number of adsorption measurements were first made in the usual way without charging the nitrogen (gas by-passed around the ionization chamber). Then, without any other alteration in the experimental conditions, the gas was diverted through the flask containing ionium salt before entering the bubbling nozzle and additional measurements of adsorption were made. Table I gives the results of two such experiments.

TABLE I

ADSORPTION EXPERIMENTS WITH RADIOACTIVE IONIZATION OF NITROGEN

	Experiment 1				Experiment 2			
Measurement	1a	1b	1c	1d	2a	2b	2c	2d
Ionization?	No	No	No	Yes	No	No	Yes	Yes
Duration, min.	11.4	17.2	13.7	9.0	18.3	16.7	17.9	14.0
Adsorption Γ (g./sq. cm. $\times 10^8$)	12.0	12.8	14.3	16.1	12.9	13.8	..	14.0

In the first experiment some difficulty was experienced in keeping bubble rate and flow of liquid properly adjusted to ensure passage of unbroken films up the short vertical drainage section of the adsorption tube. The variations in the adsorption values are therefore not more than we would expect from such a run and they do not in themselves give any indication of an effect of bubble charge on the adsorption. In experiment 2c the weight of collapsed film liquid was lost and Γ could not be calculated. The interferometer reading on this film liquid, however, indicates a value of Γ about the same as those obtained in the other experiments.

It is apparent that ionization of the nitrogen gas has had only a slight effect, if any, on the measured adsorption of *p*-toluidine. We are therefore led to the conclusion that the excessive adsorption of *p*-toluidine on moving bubbles is not due to any volume or surface electrification of the bubbles produced by their passage through the solution. This conclusion can probably be extended generally to other substances showing excessive adsorption (excessive as compared to the predicted "Gibbs" values).

Discussion

Calculation of the Effect of Surface Charge on Adsorption of Polar Molecules at the Surface of a Solution.—We shall now consider from a theoretical point of view what effect on the measured adsorption should be expected in experiments such as those described above. The ionization produced in the gas bubbles by collision of gas molecules with alpha particles consists of approximately equal numbers of positive and negative gaseous ions. Since the collisions of these ions with the bubble surface are proportional to their respective concentrations in the gas phase, approximately the same number of positive and negative ions will strike the surface in unit time. The life of any ion at the surface will depend on the nature of this surface.

In the case of *p*-toluidine solutions of the concentration used the values obtained for the adsorption of the solute (both observed values and those calculated from surface tension data) as well as the surface potential measurements of Frumkin[10] indicate that the surface being struck

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(10) Frumkin, Donde and Kulvarskaya, *Z. physik. Chem.*, **123**, 321 (1926).

consists of at least one complete layer of close-packed, vertically oriented *p*-toluidine molecules. The positive sign of the surface potential observed by Frumkin shows that the positive side of the dipole layer is directed toward the gas phase. This means that all ions striking the surface come under the influence of the local field of the positive ends of the adsorbed dipoles. The life of a negative ion in this surface is therefore probably much longer than that of a positive ion; in other words, adsorption of negative ions preponderates over that of positive ions, and the surface possesses a net negative charge. In this way a considerable electric field could be produced at the surface. In fact, if only one millionth of the surface were thus covered with adsorbed ions (10^9 ions/sq. cm.), the corresponding field strength, considered as a time average, would be

$$E = \frac{4\pi\sigma}{D} = \frac{4 \times 3.1 \times 10^9 \times 4.8 \times 10^{-10} \times 300}{80} = 22 \text{ volts/cm.} \qquad (5)$$

or somewhat more, if we use a smaller value for the dielectric constant of the surface layer. The maximum value of E, corresponding to a surface completely covered with ions of one sign, is about 22×10^6 volts/cm., or 73,000 e. s. u./cm.

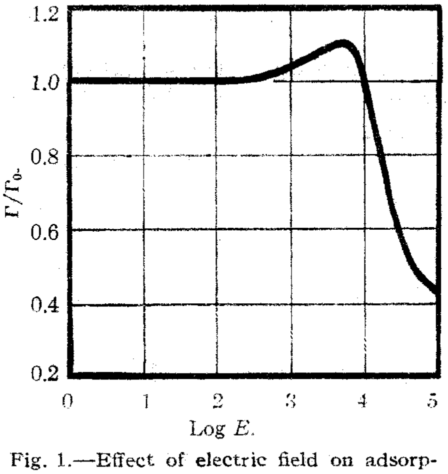

Fig. 1.—Effect of electric field on adsorption of *p*-toluidine.

The effect of an electric field on the adsorption of organic molecules has been discussed for the gas–solid interface,[11] the gas–solution interface,[12-14] and the mercury–solution interface.[15,16] None of these discussions is quite applicable to the present problem, and for our purpose we shall use a somewhat different procedure from any of these.

The potential energy of a solute molecule of dipole moment μ_s, oriented with its axis in the direction of an electric field of intensity E, is $-\mu_s E$. When one solute molecule is brought from the bulk solution into the surface layer, there are displaced v_s/v_w molecules of water (v_s and v_w represent the volumes occupied by individual molecules of solute and water). The water molecules (with dipole moment μ_w) originally in the surface layer were subject to the orienting influence of the external field, and their average moment in the direction of the field is given by

$$\bar{\mu}_w = \mu_w \times L(x) \qquad (6)$$

where $L(x)$ is the Langevin function cotgh $x - 1/x$ and $x = \mu_w E/kT$. Therefore the net work done against the external field E in bringing a solute molecule from the interior of the solution (where $E = 0$) to a vertically oriented position in the surface (where E ranges from 0 to 75,000 e. s. u./cm.) is

$$W = -\mu_s E + \frac{v_s}{v_w}\bar{\mu}_w E = -\mu_s E + \frac{v_s}{v_w}\mu_w E L(x) \qquad (7)$$

The Langevin function can be expanded in series

$$L(x) = \frac{x}{3} - \frac{x^3}{45} + \dots$$

and all terms but the first can be neglected for small values of x. That is, for all values of x up to about 1.3, corresponding to a temperature of 27° and a surface 40% covered with ions of one sign (E = 30,000 e. s. u./cm.), the net work of adsorption of one solute molecule is

$$W = -\mu_s E + \frac{v_s}{v_w}\frac{(\mu_w E)^2}{3kT} \qquad (8)$$

At sufficiently large values of E it is necessary to take into account the induced moments $\alpha_s E$ and $\alpha_w E$ of both solute and solvent molecules in the surface layer and the corresponding contributions $-\alpha_s E^2$ and $-\alpha_w E^2$ to the energies of these molecules in the electric field (α_s and α_w represent the polarizabilities of the two kinds of molecules). We shall therefore add two more terms to equation 8 and obtain the more accurate expression for the electrical adsorption work

$$W' = -\mu_s E + \frac{v_s}{v_w}\frac{(\mu_w E)^2}{3kT} - \alpha_s E^2 + \frac{v_s}{v_w}\alpha_w E^2 \qquad (9)$$

The polarizabilities can be calculated from the respective molar refractions by use of the relation

$$R = \frac{4\pi N\alpha}{3}$$

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(11) Blüh and Stark, *Z. Physik*, **43**, 575 (1927).

(12) Bradley, *Phil. Mag.*, [7] **7**, 142 (1929).

(13) Wagner, *Physik. Z.*, **25**, 474 (1924).

(14) Belton, *Trans. Faraday Soc.*, **33**, 653, 1449 (1937).

(15) Frumkin, *Z. Physik*, **35**, 792 (1926).

(16) Butler, *Proc. Roy. Soc.* (London), **A122**, 399 (1929).

If now we let Γ_0 denote the number of solute molecules adsorbed per sq. cm. in the absence of an external field, then Γ, the number of molecules adsorbed in the presence of the field, is obtained by the aid of the Boltzmann distribution law. That is

$$\Gamma = \Gamma_0 e^{-W/kT} \qquad (10)$$

where W is given by equation 9. The values of Γ/Γ_0 have been calculated for various field strengths by means of this equation; the results are given in Table II and in graphical form in Fig. 1. The following numerical values have been used for the constants of equation 9.

	p-Toluidine	Water
Dipole moment	1.65×10^{-18} e. s. u.[17]	1.85×10^{-18} e. s. u.[17]
Molar refraction	34 cc.[18]	3.6 cc.[19]
Polarizability	1.34×10^{-23} e. s. u.	1.42×10^{-24} e. s. u.
Molecular volume	192×10^{-24} cc.[20]	30×10^{-24} cc.[21]

TABLE II

EFFECT OF ELECTRIC FIELD ON THE ADSORPTION OF *p*-TOLUIDINE (TEMPERATURE 27°)

Field strength E e. s. u./cm.)	% Surface covered by adsorbed gaseous ions	Electrical adsorption work W (ergs/molecule)	Effect on adsorption Γ/Γ_0
1		-1.65×10^{-18}	1.000
10		-1.65×10^{-17}	1.000
100		-1.63×10^{-16}	1.004
755	1	-1.15×10^{-15}	1.025
1000		-1.47×10^{-15}	1.036
2000		-2.60×10^{-15}	1.065
4750	6	-3.90×10^{-15}	1.100
7550	10	-2.64×10^{-15}	1.066
10000		$+0.87 \times 10^{-15}$	0.980
75500	100	$+7.70 \times 10^{-14}$	.440[22]

Differentiation of equation 10 with respect to E shows that the function Γ/Γ_0 has a maximum at E = 4750 e. s. u./cm. and we see therefore that although the local electric field at the surface of the solution has a positive effect on the adsorption of *p*-toluidine (except at very large values of E), the increase is never more than 10%. While the above treatment of discrete charges of adsorbed gaseous ions as a continuous surface charge is admittedly somewhat simplified, the method gives an approximate average effect of such charges on the adsorption of a polar solute.

The experiments described above were completed in the chemical laboratories of Stanford University and the authors wish to thank Prof. J. W. McBain for much helpful advice. Acknowledgment is also made of the grant of a du Pont Fellowship to one of us (E. E. T.).

Summary

1. Attention is called to the fact that the adsorption of solutes at the air–solution interface, when measured by dynamic methods (moving bubbles, etc.), is generally found to be several times greater than the values calculated from surface tension data by means of the Gibbs adsorption equations.

2. In order to test the suggestion that the excessive observed adsorption is due to electrification of the moving surfaces, the authors have attempted to alter the adsorption of *p*-toluidine on moving bubbles by forced charging of the gas.

3. Marked decrease in the apparent adsorption was observed when the gas was subjected to spark discharge and to silent discharge before entering the adsorption apparatus. Because of its persistence after discharge ceased the effect was believed to be of chemical origin.

4. Ionization of the bubbling gas by exposure to ionium salt was found to have no effect on the measured adsorption.

5. The effect of a surface charge on the adsorption of polar molecules is discussed theoretically. Calculations show that the adsorption of *p*-toluidine on gas bubbles should be only slightly increased by electrification of the surface and at extreme charge densities should be somewhat decreased.

6. It is concluded that electrification of gas bubbles in contact with solutions of organic solutes is not responsible for the marked discrepancy between the observed adsorption and the calculated "Gibbs" adsorption.

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(17) C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, N. Y., 1931, pp. 67, 203.

(18) Obtained by adding the individual bond refractions[17] (p. 152).

(19) Fajans, *Naturwissenschaften*, **9**, 734 (1921).

(20) Obtained by multiplying an estimated length of 8 Å. by 24 Å.^{2}, the limiting area for condensed films of para-substituted benzene compounds found by Adam, *Proc. Roy. Soc.* (London), *A***103**, 676 (1923).

(21) Obtained from the molar volume 18 cc., divided by 6×10^{23}.

(22) For E = 75,500 e. s. u./cm. we have included the first *two* terms in the expansion of the Langevin function (equation 7) used to calculate W.