the nitric oxide or oxygen flask depending upon the initial pressures. However, no attempt was made to ensure complete dryness. The drift was observed toward either the nitric oxide or oxygen flask. Since the dimensions of the connecting tube in Stoddart's apparatus are not given, no estimate regarding the opportunity for diffusion from one bulb to the other can be made. It is likely that only a slight amount of nitric oxide entered the oxygen bulb in the cases where the initial oxygen pressures were greater than those of nitric oxide, and consequently one would not expect the appearance of much nitrogen dioxide in a short time.

Summary

1. A colorimetric method for accurately measuring the concentration of nitrogen dioxide is described for following the rate of oxidation of nitric oxide. This method, being specific for nitrogen dioxide, avoids some of the difficulties involved in the frequently employed manometric technique. It is particularly well adapted to high pressure measurements, where the rate is very rapid, and to low pressure determinations where minute amounts of nitrogen dioxide must be detected. At pressures of only a few tenths of a millimeter, nitrogen dioxide was easily detected and measured. Consequently it may be used conveniently over an extremely wide range. Data have been obtained over a 100-fold nitric oxide concentration range, at pressures ranging from approximately 0.5 mm. up to 50 mm. and at the two temperatures 0 and 25°.

2. Satisfactory agreement of the data with those previously reported was found at moderately high pressures and at low pressures where adsorption effects were eliminated. At very low pressures adsorption and surface effects were found to have a considerable influence on the reaction rate, as shown by a sharp increase in the rate constant at pressures in the range of only a few millimeters or less, particularly at the lower temperature. Such an increase was not found in the absence of an adsorbed film of nitric oxide. The results suggest that the oxidation of nitric oxide is essentially homogeneous in nature, but that adsorbed nitric oxide (and oxygen to a less extent) introduce complications at low pressures.

3. The influence of the presence of appreciable amounts of water vapor has been investigated.

4. Stoddart's observation that no reaction occurs when nitric oxide is added to a tube containing oxygen was not confirmed by the results of these experiments.

URBANA, ILLINOIS RECEIVED OCTOBER 7, 1942

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

The System Water–n-Butanol–Toluene at 30°

BY RAYMOND M. FUOSS

I. Introduction

The classical method of determining liquid–liquid equilibria by observing the appearance and disappearance of turbidity is tedious, and, for work at a fixed temperature, somewhat inconvenient. The purpose of this paper is to present a rapid method of determining liquid solubilities, using the system water–n-butanol–toluene as an example. Briefly, the method consists in adding water, containing a trace of hydrochloric acid, in successive portions to a butanol–toluene mixture of known composition. As long as the water dissolves in the organic phase, the conductance increases; with the appearance of an aqueous phase, the conductance of the organic phase drops on further addition of water, because the aqueous phase extracts hydrogen chloride from the organic phase. The saturation point is given by the cusp in the titration curve when conductance is plotted against the amount of water added.

II. Experimental Details

The butanol and toluene were redistilled C. P. products; their densities and indices of refraction checked the values given in the "International Critical Tables." About 150 g. of toluene plus butanol was weighed into a glass-stoppered Erlenmeyer flask which was then placed in a thermostat at 30.0°. A portion of water containing several tenths per cent. of hydrochloric acid was added from a weight buret and, after temperature equilibrium had been established, the conductance was measured. For the toluene-rich mixtures, a pair of lightly platinized dipping electrodes 3 × 2 cm. and 1 mm. apart were used; for the butanol-rich mixtures, where the conductance was, of course, much higher, electrodes 12 × 12 mm. and 6 mm. apart were used. Dipping electrodes must be used, because water preferentially wets the glass beads used as electrode spacers; the resulting water film shorts the electrodes and leads to erratic results. Consequently, water from the buret was added, the contents of the flask were shaken, and only after the water dissolved or after the aqueous phase settled out, were the electrodes inserted. A correction was made for the small amount of liquid which adhered to the electrodes on withdrawal at each point.

High resistances were measured on our d. c. bridge.[1] For resistances less than 100,000 Ω, we used a simple direct reading bridge consisting of two 1,000 Ω fixed resistors as ratio arms and a decade box as the bridge arm opposite the cell. Measurements were made at 10–20 volts and 1,000 cycles, using telephones as detector. No attempt at shielding was made; bridge errors and errors inherent in dipping electrodes naturally had no influence on the solubility determination, because only the location on the concentration axis of the break in the conductance curve was needed. A typical determination is shown in Fig. 1. As may be concluded from the figure, only the neighborhood of the saturation concentration is explored; the approximate location for starting was determined by several very rough preliminary measurements, in which the general course of the curve was determined.

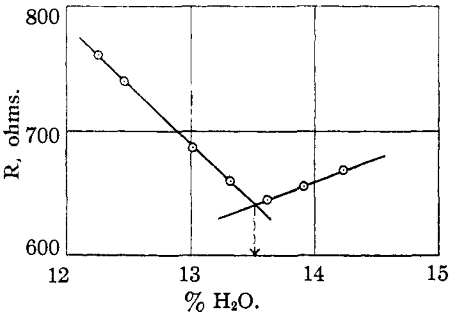

Fig. 1.—Typical titration curve.

In order to determine the composition of the aqueous phases in equilibrium with the water-saturated organic phases, a second set of experiments was made. The refractive indices of saturated organic phases made up by weight were determined at 30.0° on an Abbe refractometer and the densities were measured, using 25 cc. pyknometers. Then these constants were determined for a series of solutions of butanol in water. Water saturated with butanol at 30.0° contains 7.08% butanol[2]; the solubility of toluene in this solution as determined by the turbidity method is about 0.03%, and its effect on density and index is negligible in comparison with other experimental errors. Then mixtures of the three components were shaken together and samples taken of both phases for density and index measurements. Interpolation on large scale plots (Fig. 2) gave the composition of the two phases in equilibrium. In the organic phase, the index or density (both were used, as checks) gave the percentage of butanol, a plot of water content against butanol content gave the percentage of water, and the toluene was then determined by difference. In the aqueous phase, the toluene was neglected, and the composition was obtained by interpolation on the density and index plots for the butanol–water solutions (Fig. 3).

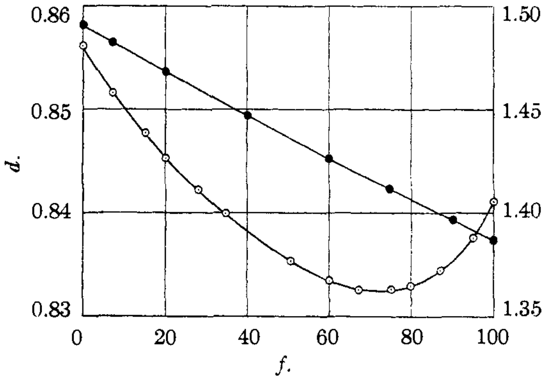

Fig. 2.—Densities (○) and indices of refraction (●) of water saturated mixtures of toluene–butanol mixtures at 30°.

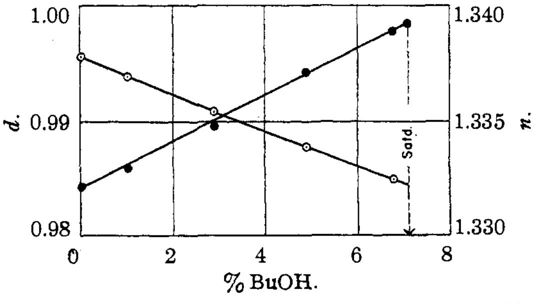

Fig. 3.—Densities (○) and indices of refraction (●) of butanol solutions in water at 30°.

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[1] Fuoss, THIS JOURNAL, **60**, 451 (1938). The batteries in the circuit of Fig. 1 have been replaced by power packs.

[2] Hill and Malisoff, THIS JOURNAL, **48**, 918 (1926).

As a cross-check, a number of more direct determinations were made, using Hill's method.[3] Two 50-cc. bulbs were connected by a 5-cc. piece of buret, and another 10-cc. length of buret was sealed to the top bulb. The volumes were calibrated by weighing water. Then weighed amounts of the three components were added to these solubility flasks in amounts chosen to bring the organic–aqueous interface into the middle calibrated section, and the top meniscus into the top buret section. Given the total weights of the three components, the volumes and densities of the two phases in equilibrium in the flask, and the composition of the organic phase from density or index, the composition of the aqueous phase could be calculated. Results obtained by the two methods were in good agreement. The direct determinations are shown as solid points in Fig. 4.

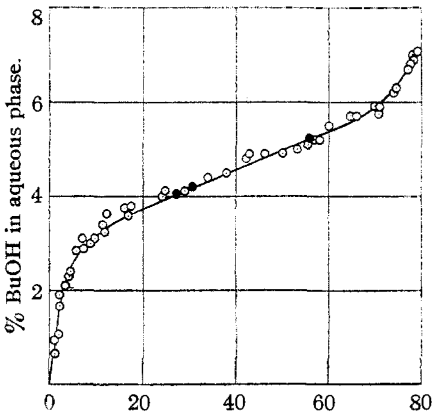

Fig. 4.—Equilibrium butanol concentrations at 30°.

III. Results and Discussion

The experimental results are summarized in Tables I–VI. Concentrations are given on two scales: f is the weight percentage of butanol in the organic components of the organic phase, *i. e.*

$$f = w_{\text{BuOH}}/(w_{\text{BuOH}} + w_{\text{PhMe}})$$

and is the directly determined experimental figure, as the above discussion of technique shows. The weight per cent. p of butanol in the total organic phase

$$p = w_{\text{BuOH}}/(w_{\text{BuOH}} + w_{\text{PhMe}} + w_{\text{H}_2\text{O}})$$

is a derived figure and depends on graphical interpolation.

TABLE I

REFRACTIVE INDICES OF BUTANOL–TOLUENE MIXTURES

% BuOH	n_{25}	n_{30}
0.0	1.4929	1.4906
20.2	1.4713	1.4690
40.0	1.4517	1.4497
58.9	1.4337	1.4320
76.9	1.4175	1.4153
100.0	1.3969	1.3953

TABLE II

REFRACTIVE INDICES OF WATER SATURATED BUTANOL–TOLUENE MIXTURES AT 30°

	p	n
0.00	0.00	1.4910
7.34	7.32	1.4824
20.00	19.77	1.4685
40.00	38.65	1.4470
59.93	56.03	1.4260
74.65	67.11	1.4113
90.00	76.14	1.3964
100.00	79.38	1.3870

TABLE III

DENSITIES OF WATER SATURATED BUTANOL–TOLUENE MIXTURES AT 30°

f	p	d	$10^4 \Delta n$
0.00	0.00	0.8562	0.3
7.34	7.32	.8516	1.3
15.05	14.94	.8477	1.5
20.00	19.76	.8453	1.8
27.98	27.45	.8422	1.4
34.79	33.85	.8399	0.8
50.48	48.00	.8354	−0.3
60.05	56.07	.8335	−1.0
67.24	61.75	.8326	−1.6
75.20	67.53	.8327	−2.9
79.88	70.61	.8330	−3.5
87.13	74.73	.8345	−4.6
94.97	77.88	.8376	−5.4
100.00	79.38	.8411	−7.3

TABLE IV

DENSITIES AND REFRACTIVE INDICES OF WATER–BUTANOL MIXTURES AT 30°

% BuOH	d	n
0.00	0.9956	1.3322
1.02	.9939	1.3330
2.89	.9909	1.3348
4.89	.9878	1.3371
6.76	.9850	1.3389
7.08	.9845	1.3392

TABLE V

SOLUBILITY OF WATER IN BUTANOL–TOLUENE MIXTURES AT 30°

p	% H_2O	f	x
19.66	1.16	19.89	0.054
19.95	1.19	20.18	.055
38.33	3.32	39.65	.138
51.01	5.50	53.98	.208
60.72	7.86	65.90	.273
67.71	10.30	75.48	.331
73.71	13.52	85.23	.398
77.24	16.44	92.44	.450
79.38[a]	20.62	100.0	.517

From ref. 2.

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(3) Hill, THIS JOURNAL, 45, 1143 (1923)

TABLE VI

TIE-LINE DATA

% BuOH in org. phase	% H_2O in org. phase	% BuOH in aq. phase
1	0.0	0.85
2	.0	1.55
3	.0	2.00
4	.1	2.35
5	.2	2.55
10	.4	3.20
20	1.2	3.75
30	2.3	4.15
40	3.5	4.55
50	5.4	5.00
60	7.8	5.40
70	11.4	5.85
75	14.9	6.35
79.4	20.6	7.10

Table I gives the refractive indices for anhydrous toluene–butanol mixtures; comparison with the data of Table II shows that the decrease in refractive index due to the water is nearly linear in the weight fraction f of butanol in the organic components. In the last column of Table III, $\Delta v = v - \Sigma v_i p_i/100$ is the difference between the actual specific volume and the volumes calculated from the composition and the specific volumes of the components, assuming additivity. An expansion occurs when butanol is added to toluene; as the butanol and water contents increase, this is followed by a contraction.

In Table V, the solubility of water in toluene–butanol mixtures is given; a plot of % H_2O–% BuOH is sharply concave up on the butanol-rich end, but a plot of mole fraction x of water against percentage of butanol in the organic components is only slightly curved, and is more accurate for interpolation. The data extrapolate to the value given by Hill and Malisoff[2] for the solubility of water in pure n-butanol.

The tie line data are given in Table VI; a smooth curve was drawn through the experimental points (Fig. 4), and interpolated values for round concentrations up to saturation are given. It will be noted that the distribution of butanol between water and toluene depends on concentration; it is such that extraction of butanol from water by toluene is not very efficient.

Summary

Equilibrium concentrations at 30° for the two-phase system of water, butanol and toluene have been determined. A new method of determining liquid solubilities is described. Densities and indices of refraction for the system are given.

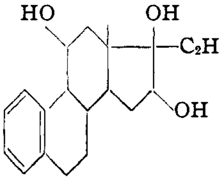
SCHENECTADY, N. Y. RECEIVED OCTOBER 13, 1942

[CONTRIBUTION FROM THE DEPARTMENTO DE QUIMICA DA FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS DA UNIVERSIDADE DE SÃO PAULO, BRAZIL]

Cafesterol. II[1]

BY HEINRICH HAUPTMANN AND JANDYRA FRANÇA[2]

Slotta and Neisser[3] isolated cafesterol from the unsaponifiable fraction of coffee oil and proposed formula I for its structure. The results of our experiments of the past few years[1] led us to suggest formula II, in which there are two olefinic double bonds (and no benzenoid ring), a non-reactive keto group, and a —C(OH)CH_2OH group.



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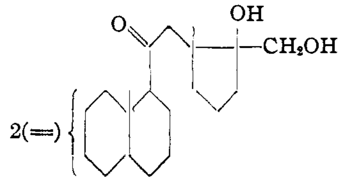

II

It must be admitted that the steroid skeleton and the position of the groups are hypothetical. Moreover, the question remains open as to whether there is present a non-reactive keto group or an oxide ring.

Recently, Wettstein, Fritzsche, Hunziker and Miescher[4] proved that the two double bonds in cafesterol are conjugated by the preparation of an addition product with maleic anhydride. By an independent method they also established the presence of a —C(OH)CH_2OH group, and located it next to a methylene group in a five-mem-

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(1) Paper I, *Z. physiol. Chem.*, **259**, 245 (1939).

(2) The results of this paper are in large part taken from a thesis submitted to the *Faculdade de Filosofia, Ciências e Letras de Universidade de São Paulo*, Brazil, by Jandyra França on April 15, 1941, in partial fulfillment of the requirements for the degree of Doctor of Science. The examination and discussion of the thesis were delayed due to administrative reasons, until March 23, 1942. As the law allows only unpublished theses, we were forced to postpone the publication of this paper.

(3) Slotta and Neisser, *Ber.*, **71**, 1991, 2342 (1938).

(4) Wettstein, Fritzsche, Hunziker and Miescher, *Helv. Chim. Acta*, **24**, 332 (1941). We received this issue on June 23, 1942.