chemical data ("International Critical Tables") is −38,600 cal.

Summary

The equilibrium between pyridine, hydrogen and piperidine has been measured at 150 and at 170°, and more approximately at 180°. The heat of reaction and the accompanying free energy changes have been calculated.

BURLINGTON, VERMONT RECEIVED JULY 15, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

Diffusion Coefficients in Alcohol–Water Mixtures

BY H. MOUQUIN AND W. H. CATHCART

The diffusion coefficients of a number of organic dyes dissolved in water–ethyl alcohol mixtures of varying composition were studied by Ostwald and Quast.[1] Their method, which essentially involves a continuously varying diffusion layer, seemed to contain some experimental difficulties. In view of this fact and the rather unusual nature of their results, the present authors attempted to repeat the original experiments with the intention of extending the work in this field. In spite of every effort to duplicate the conditions described in the original paper, the method proved too unreliable to permit verification of the previous findings.

The Ostwald method contained two obvious limitations: first, the solutions were placed in an unsealed vessel and were thus very sensitive to any disturbances capable of bringing about mass flow; second, the arrangement of the apparatus was such that it necessarily involved the tacit assumption that the density of the solution was greater than that of the solvent.

Testing the relative densities of crystal violet solutions and corresponding solvents at varying alcohol concentrations by means of the "schlieren" method, it was soon discovered that at least in the region between 25 to 50% (by weight) of alcohol the density of the 0.1% dye solution was actually less than that of the corresponding solvents. This no doubt is the major difficulty involved in the Ostwald method.

In recent years, a method first used for the measurement of diffusion coefficients by Northrup and Anson,[2] and greatly extended by McBain and co-workers, has become available. We refer to the so-called fritted glass membrane method, involving a constant diffusion-layer thickness. In two recent papers, McBain and Dawson[3] have pointed out the advantage of using a closed system. In a previous paper,[4] the disadvantages of stirring had been mentioned, but this was attempted only in an open cell.

The major requirements in the membrane cells not only include the existence of an undisturbed diffusion gradient in the membrane, but also adequate stirring in the bulk of the solutions right up to the surface of the fritted glass disk. If this last condition is not fulfilled, secondary diffusion layers build up beyond the strict confines of the membrane and this introduces a variable and unknown factor.

In the original technique, density difference between solvent and solution must be depended upon entirely for adequate mixing. Variations in viscosity must certainly affect the efficiency of this gravitational streaming, but, besides this, the density differences can vary over a wide range from case to case.

In the case at hand where the density differences may become vanishingly small, it is obvious that the traditional technique is impossible. In fact the formation of vague secondary diffusion layers beyond the physical boundaries of the membrane could easily be seen in the case of the more highly colored solutions.

The cell shown in Fig. 1 was designed to overcome the above difficulties and has been in use in this Laboratory for more than a year. First, it is entirely enclosed;[3] this effectively prevents any mass flow, outside of the most violent agitation. Second, the entire cell is slowly rotated at a speed somewhat under one r. p. m. by means of a wheel and belt drive placed in the thermostat. This motion coupled with the rise and fall of the en-

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(1) Ostwald and Quast, *Kolloid-Z.*, **48**, 83–95 (1929); **51**, 273 (1930).

(2) Northrup and Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

(3) McBain and Dawson, THIS JOURNAL, **56**, 52 (1934); also *Proc. Roy. Soc.* (London), **A148**, 32 (1935).

(4) McBain and Liu, THIS JOURNAL, **53**, 59 (1931).

closed glass balls brings about gentle but sufficient mechanical stirring right up to the membrane surface.

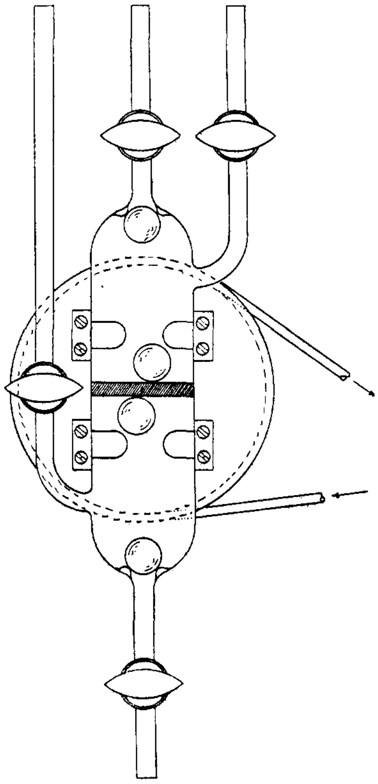

Fig. 1.

A few more practical details may be useful to other workers. One of each pair of glass balls is light enough to float, while the other sinks. The relative buoyancy of these, as well as the rate of rotation, should not be exaggerated, since the resultant excessive wear and tear tends to form a groove on the friable glass disk. Attempts to substitute mercury globules for the glass spheres have yielded unsatisfactory results. Indentations in the cell walls, near the ends, prevent the balls from blocking the end-tubes while the solutions are being removed. If sufficiently large stopcocks are used (6 mm. or more) and the solutions are of ordinary viscosity, the side tubes shown may be dispensed with. As in former methods, one end of the cell and the membrane are first filled by suction and the usual routine of refilling, etc., carried out before starting the rotation.

The effect of the stirring is at once evident when the cell constant of the rotating cell is compared with the same cell in a stationary position. As determined according to McBain, with 0.1 N hydrochloric acid, the constant in the cell used here showed an increase of nearly 5% when adequate stirring was maintained.

The data given in Table I show the diffusion coefficients of crystal violet taken over the whole range of water–alcohol mixtures, as obtained by this method. Curve II on Fig. 2 shows the data plotted graphically. Curve I is taken from Ostwald's data for comparison. The crystal violet was a very pure sample obtained from Grübler which has proved satisfactory in other research carried out in this Laboratory. The original solutions contained 0.1 g. of the monohydrate dye in 100 cc. of the solvent mixtures; the changes in concentration were measured by known dilution of the original solution until a close match was obtained in the colorimeter. The thermostat was kept at 25° and the viscosity corrections were made relative to water at that temperature. In verifying the fact that there is no appreciable difference in the viscosities of solvent and corresponding solution, the results seemed to be in bet-

Table I

Data with Present Cell

Rotating cell constant = 0.066/day

Wt. % alcohol	$D \times 10^6$ (diffusion coefficient/sec.)			Av. value (corr. for viscosity)
0.00	7.48	7.68	7.48	7.55
15.48	4.41	4.44		8.18
26.76	3.62	3.68		8.54
40.58	3.36			8.90
49.62	3.49	3.54		9.28
55.31	3.68	3.62		9.43
61.84	3.98	3.92		9.71
67.51	3.69	3.69		8.58
71.16	3.30	3.20		7.25
80.62	3.63			6.90
94.75	4.26	4.31	4.35	6.11

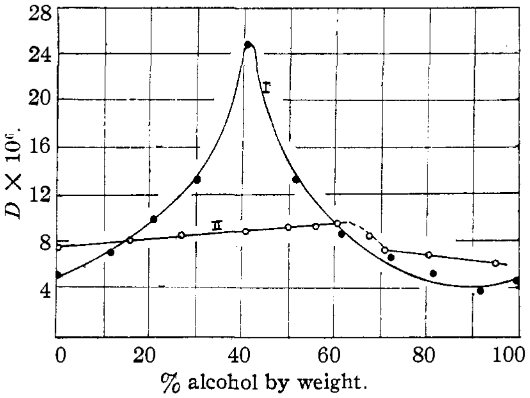

Fig. 2.

ter agreement with those published by Butler[5] than with the data given in the "International Critical Tables;" accordingly, the former were used to make the corrections.

Compositions of the water–alcohol mixtures were checked by determining the density by means of a pycnometer and tables given in "I. C. T."

The most interesting region of the curve consists of a definite "break" observable in the vicinity of 65 wt. % alcohol. Robinson and co-workers[6] have shown that it is seldom justifiable to interpret data for electrolytes such as given above, in terms of particle sizes. In any case some primary cause for the sharp break would have to be accounted for.

Since the days of Mendeléjeff attempts to furnish evidence of compound formation in alcohol–water mixtures have not been very successful. If we now take the break at 65 wt. % of ethyl alcohol as such evidence we are immediately confronted with the fact that this composition does not correspond to a one-to-one or any other whole number ratio of the traditional molecular weights. This criticism becomes less destructive when it is realized that the ratio of the two molecular weights in the liquid state of such compounds is not definitely known. If we assume the molecular weight of the alcohol to be normal, and that 65% corresponds to a one-to-one compound tendency it is necessary to assume an average molecular weight for water of about 25. A fairly reliable and independent substantiation of this value is to be found in the calculations made by Murray[7] based on the vapor pressure data obtained by Makowiecki for acetone–water mixtures.

Further search revealed a considerable quantity of evidence suggestive of the peculiar significance of the 65% region. If we restrict ourselves to the mixtures (neglect values for pure water and 100% alcohol), plotting various sorts of physical properties against the weight percentage very frequently demonstrates an abrupt change in the character of the solvents at this particular composition. In some cases, this is best revealed by a logarithm plot.

TABLE II

A. C. RESISTANCES OF THE ORIGINAL SOLUTIONS (CELL CONSTANT 1.3943)

% alcohol by wt.	$R \times 10^{-3}$ resistance (ohms)	$\eta^{25°}$ compared to H_2O	$R/\eta^{25°} \times 10^{-3}$
15.48	11.30	1.75	6.47
30.50	14.36	2.45	5.86
40.58	18.20	2.66	6.84
49.61	19.17	2.64	7.25
55.30	19.00	2.57	7.39
61.84	19.77	2.47	8.00
67.50	19.37	2.33	8.31
71.16	19.57	2.22	8.82
80.62	20.00	1.92	10.41
94.75	19.76	1.43	13.80

Figure 3 shows the plot of Table II, which is the electrical resistances, corrected for viscosity, of the crystal violet solutions used in the diffusion experiments. (The dye contains less than 0.5% sodium chloride.) A "break" around 65% is noticeable. A similar effect can be seen by making a log plot of the conductivity data (viscosity correction) published[5] for zinc chloride and potassium iodide solutions.

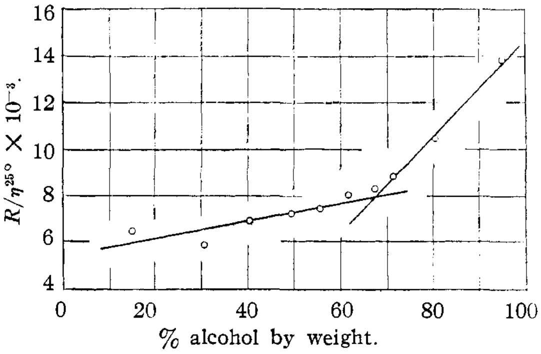

Fig. 3.

Other data which show irregularities in the 65% region are (1) log plot of the solubilities of zinc valerate, phenyl salicylate, ammonium benzoate, lithium benzoate and others (data from "I. C. T."); (2) log plot of % deviation of kinematic viscosity from a linear additivity rule (data from "I. C. T."); (3) dielectric constant for water–ethyl alcohol mixtures (plot on large scale).[8]

From the above evidence it seems fairly clear that the observed break in the diffusion coefficient must be caused by a peculiar condition characteristic of this solvent mixture.

Summary

1. The inadequacies of some former diffusion measurements are pointed out.

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(5) Connell, Hamilton and Butler, *Proc. Roy. Soc.* (London), **A147**, 418–423 (1934).

(6) Hartley and Robinson, *ibid.*, **A134**, 20 (1931); Robinson, *Soc. Dyers and Colourists*, p. 161 (June, 1934); Robinson, *Proc. Roy. Soc.* (London), **A148**, 881 (1935).

(7) Murray, *J. Phys. Chem.*, **33**, 904 (1929).

(8) Åkerlöf, THIS JOURNAL, **54**, 4130 (1932).

2. A new technique is developed and described.
3. The diffusion coefficients of crystal violet in alcohol-water mixtures are determined.
4. A possible explanation for an observed break in the regularity of the experimental curve is suggested.

NEW YORK, N. Y. RECEIVED AUGUST 1, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL]

Studies in the Physical Chemistry of Amino Acids, Peptides and Related Substances. V. Influence of Amino Acids, Urea and Alcohol upon the Velocity Constants of Chemical Reactions[1]

BY DANELLA STRAUP AND EDWIN J. COHN

The velocity constants of most chemical reactions are not independent of changes in the medium but vary with the ionic strength and the dielectric constant. The variation with change in salt concentration appears to be explained adequately by Brönsted's[2] theory of reaction rates, which considers the rate proportional to the activity coefficients of the reactants and inversely proportional to the activity coefficient of the critical complex. In the present communication we are concerned with the influence of alcohol, urea and amino acids upon reaction rates. All of these substances profoundly influence the dielectric constant of the medium and their activity coefficients vary in a very different manner from those of electrolytes.

In dilute electrolyte solution activity coefficients, and therefore changes in reaction rate, may be estimated by means of the Debye limiting law. The effect of more concentrated electrolytes or of non-electrolytes may be calculated by the method of Christiansen.[3] This method has been recently discussed by Harned and Samaras,[4] La Mer[5] and Scatchard.[6] The Brönsted–Christiansen and Debye–Hückel theories yield[6]

$$\log \frac{k}{k_0} = \frac{\epsilon^2 Z_A Z_B}{2.303\, DKT} \frac{\kappa}{1 + \kappa a} \qquad (1)$$

in which k is the velocity constant in the salt solution, k_0 that in the absence of salt, K is the Boltzmann constant, κ the reciprocal distance proportional to the square root of the ionic strength, and a the distance of closest approach of the ions. The velocity constant should vary, according to equation (1), not only with the valence, Z, and ionic strength, μ, of the electrolytes, but with any change in the dielectric constant[7] of the solution, D, from its value in the standard state, D_0. Signifying by k' the velocity constant at zero ionic strength in a medium having a dielectric constant other than that of the standard state, equation (1) may be written

$$\log \frac{k}{k'} = \frac{Z_A Z_B\, (D_0/D)\, \sqrt{(D_0/D)\mu}}{1 + (a/3)\, \sqrt{(D_0/D)\mu}} \qquad (2)$$

When D is equal to D_0, k' is equal to k_0.

The effect of changing dielectric constant on reactions between ions at zero ionic strength has been calculated[6] as

$$\log \frac{k'}{k_0} = \frac{\epsilon^2 Z_A Z_B}{2.303\, KTa} \left(\frac{1}{D} - \frac{1}{D_0}\right) = \frac{242.3\, Z_A Z_B}{a} \left(\frac{1}{D} - \frac{1}{D_0}\right) \qquad (3)$$

This equation is analogous to the Born–Fajans equation for equilibrium relations.

Amino acids, due to their zwitterionic structure, exert electrostatic forces in solution. Since they do not contribute to the ionic strength, Debye's equation does not apply even in dilute solution. Solutions of amino acids have high dielectric constants and attempts have been made to describe the effect of amino acids on activity coefficients[8] in terms of the Born–Fajans equation. Another treatment of the effect of amino acids is described later on in this paper.

Two types of reactions have been studied: (1) a reaction between a non-electrolyte and an ion, and (2) a reaction between two ions. The thio-

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[1] A preliminary account of this investigation was read to the Society of Biological Chemists [*J. Biol. Chem.*, **105**, Proc. 87 (1934)].

[2] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925); Brönsted and Livingston, THIS JOURNAL, **49**, 435 (1927).

[3] Christiansen, *Z. physik. Chem.*, **113**, 35 (1924).

[4] Harned and Samaras, THIS JOURNAL, **54**, 9 (1932).

[5] La Mer, *Chem. Rev.*, **10**, 179 (1932).

[6] Scatchard, *ibid.*, **10**, 229 (1932).

[7] The dielectric constants of the solvents employed have been determined by Wyman [THIS JOURNAL, **53**, 3292 (1931); *ibid.*, **55**, 4116 (1933)]. In dilute solution they have been estimated by the equation: $D = D_0 + \delta C$, where D_0 is 78.54 at 25°, δ is 2.8 for urea, 22.7 for α-, and 36 for β-amino acids [Wyman and McMeekin, *ibid.*, p. 908].

[8] Failey, *ibid.*, **54**, 576 (1932).