for twenty-two substances investigated by seven authors. This value is the general average from data where the deviations from unity do not exceed the experimental errors. It should be emphasized that other investigators[9] have reported exchange constants that differ from unity by as much as 50%. For this reason calcium hydroxide was investigated. A sample of D_2O ($F_D = 0.1900$) was treated with calcium oxide and the density of the solvent showed a slight increase ($F_D = 0.1909$). The reaction involved is

$$CaO + (H_2O\text{-}D_2O) = \{Ca(OH)_2 - Ca(OD)_2\}$$

and the equilibrium is

$$D_2O + Ca(OH)_2(xD_2O) = H_2O + Ca(OD)_2(xD_2O)$$

Table VII shows the results of the determination and the calculated value of the exchange constant, $K = 0.83$. This corresponds to a value of $\alpha = 0.91$.

Summary

The equilibrium process $^1/_2H_2O + KOD(D_2O) + KBr(H_2O) = {}^1/_2\,D_2O + KOH(H_2O) + KBr(D_2O)$ has been determined from analytical measurements of the process $^1/_2HgO(s) + {}^1/_2Hg(l) + {}^1/_2H_2O + KBr(H_2O) = {}^1/_2Hg_2Br_2(s) + KOH(H_2O)$ in H_2O–D_2O mixtures and found to compare favorably with the value calculated by indirect means. Four temperatures, 20, 25, 30 and 35°, have been investigated using protium oxide and three temperatures, 20, 25, 30° using deuterium oxide. From the temperature coefficients the several thermodynamic functions were calculated.

The importance of the difference between exchange and transfer free energy has been emphasized for the purpose of clarifying statements appearing in the literature.

The solubilities of thallous chloride and calcium hydroxide have been determined in the two waters at 25° and the exchange coefficient of the base measured in a sample of mixed solvent.

A series of transfer equilibrium constants have been obtained from solubility measurements in this investigation and others calculated from existing data.

An indirect means has been developed for calculating the ion product constant of deuterium oxide. The value obtained was 1.54×10^{-15}, in good agreement with the value reported by Abel, Bratu and Redlich.

Finally it has been shown that in equilibria in mixtures of H_2O–D_2O both the free energy of transfer and the free energy of exchange are contributing factors but in many cases the latter is of minor importance.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Surface Tension of Solutions of Electrolytes as a Function of the Concentration. III. Sodium Chloride

BY GRINNELL JONES AND WENDELL A. RAY

Prior measurements of the relative surface tensions of solutions of some eleven salts have in each case shown the existence of a minimum in the surface tension–concentration curve at extreme dilution.[1] Similar measurements have now been carried out with sodium chloride at 25° over a concentration range of 0.0001 up to 2 molar.

The sodium chloride (Mallinckrodt analytical reagent grade) was purified by twice precipitating with hydrogen chloride, washing and drying the crystals by centrifugation and, finally, by drying and fusing in a platinum dish. The resulting salt was not hygroscopic. A saturated solution showed no red coloration with phenolphthalein. The density measurements, made by means of two 50-ml. Ostwald type pycnometers, gave duplicate results, differing by no more than a few parts per million. The measurements, which were made by the differential capillary rise method, give the "apparent relative surface tension" as defined on page 291 of the second paper of this series, and are the mean of at least two independent determinations which usually differed by no more than a few thousandths of a per cent.

These results are given in Table I and are shown graphically in Figs. 1 and 2.

Interpretation of the Data.—The densities of sodium chloride can be expressed over the range

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[1] Grinnell Jones and Wendell A. Ray, THIS JOURNAL, 59, 187 (1937); 63, 288 (1941); Grinnell Jones and L. D. Frizzell, *J. Chem. Phys.*, 8, 986 (1940).

TABLE I

Concentration, molar	Density, d^{25}_4	Apparent relative surface tension, σ_c/σ_0	$(\sigma_c - \sigma_0)/c\sigma_0$
0.000100	0.997078	0.99995	−0.5
.000200	.997082	.99990	− .5
.000500	.997093	.99991	− .18
.001000	.997110	.99990	− .09
.002000	.997148	.99997	− .015
.005000	.997282	1.00014	+ .028
.010000	.997483	1.00034	+ .034
.020000	.997898	1.00068	+ .034
.050000	.999138	1.00153	+ .031
.10000	1.001193	1.00280	+ .0240
.20000	1.005277	1.00538	+ .0269
.50000	1.017357	1.01254	+ .02508
.99998	1.037065	1.02421	+ .02421
1.99962	1.075294	1.04819	+ .02410

studied by an equation of the form suggested by Root[2]

$$d^{25}_4 = 0.997074 + 0.041882c - 0.001878c^{3/2}$$

This equation agrees with the data with an average deviation of about 0.001%.

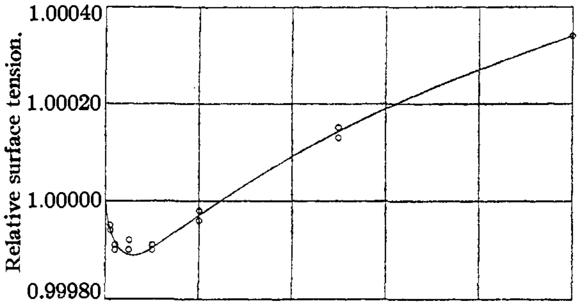

Fig. 1.

The values in the last column of the table for $(\sigma_c - \sigma_0)/c\sigma_0$ should be constant if Quincke's rule were valid. This is not the case; instead it is evident from the curve that the relative surface tension in the extreme dilute range becomes less than unity giving a minimum in the surface tension-concentration curve, similar to the minimum previously found by us for eleven other salts. The surface tension at the minimum is about 0.011% less than that of water and it occurs at a little less than 0.001 molar.

From 0.005 to 2 molar the surface tension is nearly a linear function of concentration, as was first suggested by Quincke. The slight curvatures are similar to those previously reported for other salts.

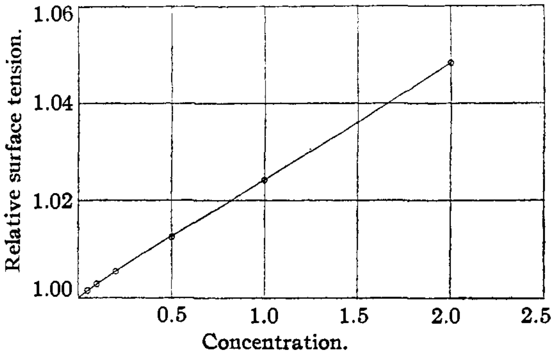

Fig. 2.

Summary

The relative surface tensions of aqueous solutions of sodium chloride have been measured from 0.001 to 2 molar at 25°.

At extreme dilution sodium chloride, like all of the salts so far reported in this series, gives a minimum in the surface tension–concentration curve and therefore behaves as a "capillary-active" substance.

At moderate and high concentrations sodium chloride acts like a typical "capillary-inactive" salt increasing the surface tension of water slightly and almost linearly with increasing concentration.

CAMBRIDGE, MASSACHUSETTS RECEIVED AUGUST 27, 1941

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(2) W. C. Root, THIS JOURNAL, **55**, 850 (1933).