previously described. At 28° there was no indication of active hydrogen.

Anal. Calcd. for $C_{23}H_{23}N$: C, 88.34; H, 7.40; mole of active H, 1.00. Found: C, 88.26; H, 7.45; moles of active H, 1.05.

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Dielectric Constant and Refractive Index from 20 to 35° and Density at 25° for the System Tetrahydrofuran–Water[1]

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For studies of conductance, activities and rates of reaction in solution it is desirable to have available solvent mixtures which may be made up to any specified dielectric constant within a wide range of dielectric constant values. To know to what extent the effects measured are functions of the dielectric constant only, and not of the specific solvent mixture used, it is necessary to use different mixtures to cover the same range of dielectric constant. Dioxane–water, methanol–water and other mixtures have been used for such studies. The system tetrahydrofuran–water is proposed as an alternate solvent system for these studies. The dielectric constant of tetrahydrofuran is relatively low and it is miscible with water in all proportions. Tetrahydrofuran of high purity is now available commercially. For the tetrahydrofuran–water system we report here the dielectric constants and refractive indices from 20 to 35° and the densities at 25°.

Experimental

Materials.—The water used in these measurements was prepared as described previously.[4] The fraction retained had a specific conductance of 1×10^{-6} ohm^{-1} cm.$^{-1}$. The tetrahydrofuran, from the Electrochemicals Department of E. I. du Pont de Nemours and Co., contained hydroquinone as an inhibitor. The tetrahydrofuran was separated by distillation after being mixed with an equal volume of heavy mineral oil to prevent an accumulation of concentrated peroxides in the still. For the product thus obtained, time–temperature cooling curves were determined using an N.B.S. calibrated platinum resistance thermometer and a Leeds and Northrup Co. Mueller Bridge. The freezing point was found to be −109.238° and the purity, as determined from the shape of the curves by the method of Rossini,[5] was found to be not less than 99.87%. This purity was adequate for the present purpose and so no further purification was attempted.

Method.—The measurements of dielectric constant were made with the apparatus previously described[4] except that a larger inner electrode was used in the cell. The cell was calibrated at each temperature used, since the cell capacitance was relatively large and small changes in the dimensions of the cell with temperature variations caused slight variations in cell capacitance. For calibration of the cell, the dielectric constant of water at the various temperatures was assumed to be as reported by Wyman[6] and Albright.[7]

Table I lists for the various temperatures the capacitance of the cell containing water, the dielectric constant of water with the corresponding literature reference, the calculated cell capacitance, $d\epsilon/dc$, and the lead capacitance.

TABLE I

CALIBRATION DATA FOR NON-INDUCTIVE TYPE CELL

Temp., °C.	Cell capacitance with water	Dielectric constant of water	Cell capacitance	Lead capacitance
20	390.13	80.38	4.836	1.41
25	381.66	78.48	4.846	1.35
30	372.76	76.75	4.839	1.37
35	363.05	74.95	4.825	1.42

In order to check this calibration, the dielectric constants of methanol and acetone were determined at 25°. The value, 20.74, which was obtained for acetone agrees exactly with the value given by Albright,[7] and the value, 32.66, which was obtained for methanol is in exact agreement with the value of Albright and Gosting.[8]

A Bausch and Lomb Abbé refractometer was used for the refractive index measurements. The density determinations were made by the usual method using a 50-ml. Leach specific gravity bottle, fitted with a thermometer by means of a ground glass joint. This pycnometer was filled and the liquid level was adjusted in a constant temperature-bath which was controlled within 0.01°. All density calculations were based upon the density of water at 25°.

Results

The dielectric constants for the system tetrahydrofuran–water from 20 to 35° are shown in Table II. These data are believed to be accurate to about one part in 1000 in the low range of dielectric constant and one part in 2000 at the higher range.

TABLE II

DIELECTRIC CONSTANT FOR THE TETRAHYDROFURAN–WATER SYSTEM

	Temperature, °C.			
THF, wt. %	20	25	30	35
0.00	80.37	78.48	76.75	74.95
10.00	73.73	71.76	70.15	68.68
20.00	66.46	64.60	63.02	61.64
30.00	58.42	56.59	55.24	53.88
40.00	49.77	48.22	46.91	45.65
50.00	41.21	39.96	38.77	37.75
60.00	33.04	31.97	31.04	30.24
70.00	25.45	24.62	24.08	23.39
80.00	18.75	18.25	17.77	17.38
90.00	12.90	12.59	12.36	12.05
95.00	10.24	9.97	9.74	9.58
100.00	7.58	7.39	7.25	7.16

Table III shows the refractive indices for the system tetrahydrofuran–water over the temperature range 20 to 35°.

The absolute densities of the tetrahydrofuran–water system were determined at 25°. The density of water was taken as 0.9970 and the density of the tetrahydrofuran was measured to be 0.8811 at this temperature. The intermediate densities may be calculated by the equation

$$d = 0.9970 - 2.582 \times 10^{-4}P - 1.074 \times 10^{-5}P^2 + 1.73 \times 10^{-8}P^3$$

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[2] The data upon which this report is based are included in the Ph.D. Dissertation of Frank E. Critchfield, West Virginia University, 1953.

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TABLE III

REFRACTIVE INDEX FOR THE TETRAHYDROFURAN–WATER SYSTEM

THF, wt. %	Temperature, °C.			
	20	25	30	35
0.00	1.3330	1.3324	1.3320	1.3314
10.00	1.3433	1.3427	1.3419	1.3412
20.00	1.3537	1.3527	1.3519	1.3510
30.00	1.3637	1.3622	1.3611	1.3600
40.00	1.3724	1.3711	1.3695	1.3683
50.00	1.3801	1.3788	1.3769	1.3753
60.00	1.3872	1.3854	1.3837	1.3819
70.00	1.3934	1.3915	1.3896	1.3878
80.00	1.3987	1.3967	1.3949	1.3938
90.00	1.4033	1.4011	1.3989	1.3967
95.00	1.4050	1.4028	1.4008	1.3986
100.00	1.4068	1.4045	1.4022	1.4000

where d is the density and P is the weight % of tetrahydrofuran. Densities calculated using this equation agree with the experimental values within 2 parts in 10,000.

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The Heats of Neutralization of Acid Clays and Cation-exchange Resins[1]

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A note of considerable interest to soil scientists and others concerned with the chemical reactions of clays and other ion-exchange materials was recently published.[2] The author reported the heats evolved when acid bentonites prepared by electrodialysis and by passage through a column of H-sulfonic acid exchange resin were neutralized with NaOH. Also presented were potentiometric titration curves of clays prepared by the two procedures. Up to about 80% base saturation the freshly-columned clay gave a titration curve of strong acid character, similar to that of H-sulfonic acid exchange resins. At this point a sharp inflection was followed by a short region of buffering in the *p*H range 6–7, and then a second inflection. The heat of neutralization in the first portion of the titration curve was about −13.5 kcal. per mole, again indicating strong acid character.

In the case of electrodialyzed clay the initial strong acid portion of the potentiometric titration curve extended to only about 30% base saturation, while the region of buffering between *p*H 6 and 7 was pronounced. The heat of neutralization in the strong-acid portion of the curve was again about −13.5 kcal. per mole. This fell to around −5 kcal. in the *p*H range 6–7. Slabaugh has explained the heats and the course of the titration curves on the basis that two H-ion energy levels exist.

The present authors have made similar observations on a variety of clay and exchange resin systems, and have come to somewhat different conclusions. Clays of the montmorillonite type, of which Slabaugh's Wyoming bentonite is typical, are alumino silicates. It is well established that in slightly acid media such clay minerals decompose with the liberation of ionic aluminum.[3] Such ionic aluminum appears to be strongly adsorbed by the clay, with the result that acid clays prepared by electrodialysis, by dilute acid leaching, or by natural depletion of such cations as Ca and Mg in nature, contain both H and Al as exchangeable cations with the latter usually predominating.[3-5]

It is possible, however, as Slabaugh[2] has pointed out, to prepare acid clays which differ greatly from those obtained by more conventional means. Columning with H-exchange resin is one method by which this may be done. Rapid leaching with 1 *N* HCl also results in a clay with the electrochemical and thermochemical properties of columned clay. For the reasons outlined below, the present authors believe columned clay and 1 *N* HCl-leached clay to be H-clays, while electrodialyzed and dilute acid leached clays are H-Al-clays.

Figure 1 shows potentiometric titration curves of H- and Al-Amberlite IR-120, acid bentonite prepared by leaching with 0.1 *N* HCl, and acid bentonite prepared by leaching with 1 *N* HCl. Figure 2 compares the curve for acid bentonite prepared by leaching with 1 *N* HCl with those for bentonite leached first with 1 *N* HCl and then with $AlCl_3$, and bentonite leached with 1 *N* HCl and treated with an amount of $AlCl_3$ equivalent to one-half the exchange capacity. In all cases free electrolyte was removed by washing with water before the titrations were performed. The similarity between the curves for Al-resin, dilute acid-leached clay, and $AlCl_3$-leached clay is striking. Also very similar are the curves for H-resin and 1 *N* HCl-leached clay. The 1 *N* HCl-leached clay treated with $^1/_2$ symmetry concentration of $AlCl_3$ shows the features of both H- and Al-exchangers, with the H being neutralized first.

Heats of neutralization of several clay and exchange resin systems are presented in Table I. They were measured with an apparatus which has been described previously.[6] The heats reported in Table I are integral rather than the summation of differential heats as measured by Slabaugh,[2] and refer in all cases to the amount of NaOH consumed in the reaction. Heats of neutralization of H-exchange resins and of columned or 1 *N* HCl-leached bentonite were about −13.5 kcal., which is close to the heat of formation of water from the ions. Heats of neutralization of the Al-resin and

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