of the dimer (or possibly mixture of dimers) encountered here, and that met with in the butadiene experiment.

Acknowledgment.—The author is pleased to acknowledge his indebtedness to the Gates Laboratory for the hospitality and facilities extended him, and to his associates there for aid during his stay in Pasadena.

Summary

The homogeneous thermal polymerization of isoprene has been investigated in the temperature range of 286.5 to 371° at pressures varying from 212 to 739 mm.; the principal process is interpreted as a bimolecular association reaction, the rate of which is expressible by $k = 2.19_3(10^{10}) T^{1/2}e^{-28,900/RT}$.

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Dielectric Constants: Ethanol–Diethyl Ether and Urea–Water Solutions between 0 and 50°

BY JEFFRIES WYMAN, JR.

The importance of a knowledge of the dielectric constant of the solvent as well as its change with temperature in the study of solutions is well known and requires no elaboration. The present paper is a report of routine measurements at a variety of temperatures on two sets of solvents of considerable use especially in organic and biological chemistry. The first set, consisting of mixtures of ethanol and diethyl ether, covers a range of dielectric constant from about 4 to 28. The second, comprising aqueous solutions of urea of concentrations running up to nearly 8 moles per liter, is characterized by dielectric constants greater than that of water, in fact approaching 108 at the upper limit. In this respect the urea–water solutions occupy an exceptional position and afford a convenient class of solvents of high dielectric constant. In fact, apart from certain ampholytes supposed to exist as zwitter ions and one or two compounds closely related to it, urea is the only substance known to form solutions of dielectric constant greater than that of water.[1] Existing data on the dielectric constant of both the above sets of liquids are somewhat incomplete and contain inconsistencies. The present results serve to extend the list of mixed solvents of accurately known dielectric properties such as those dealt with in recent papers by Åkerlöf[2] and Wyman.[3]

[1] See Devoto, *Gazz. chim. ital.*, **61**, 897 (1932); also Wyman and McMeekin, THIS JOURNAL, **55**, 908 (1933); **55**, 915 (1933).

[2] Åkerlöf, *ibid.*, **54**, 4125 (1932).

[3] Wyman, *ibid.*, **53**, 3292 (1931).

The values given in the present investigation were obtained by an absolute method, were reproducible to better than 0.1%, and, it is believed, are entirely free from systematic errors. The principle underlying this method consists in determining the electrical resonance point of a small metal circuit completely immersed in the dielectric to be measured. The dielectric constant in question is equal to the square of the ratio of this resonant wave length divided by the resonant wave length of the same circuit in a vacuum, or, in practice, in air.[4] The size of the resonant circuit required for use at a given wave length increases rapidly with decrease in the dielectric constant. In the case of the alcohol–ether mixtures the circuit required for use at convenient wave lengths is considerable and would ordinarily involve more than a liter of liquid for adequate immersion to include the entire field. For this reason a special type of resonator built up of concentric cylinders and having a very small stray field was employed. This circuit necessitated the use of less than 100 cc. of solution for satisfactory immersion and at 25° resonated at 8.612 meters in pure ether and at 20.69 meters in pure alcohol. A description of this form of resonator has been given elsewhere.[5]

In order to make sure that no systematic errors were introduced by the use of such small amounts of liquid, owing to the stray field of the resonator not included in the liquid, a careful comparison was made of the dielectric constant of a sample of alcohol at 25° determined in one case with the resonator immersed in a large volume of liquid and in the other case with the resonator in a small tight-fitting glass vessel containing about 75 cc. and jacketed with circulating water drawn from the thermostat. The two values obtained for the dielectric constant were 24.32 and 24.33, respectively, the difference being no greater than the experimental error of the determinations.

In the case of the urea–water solutions, owing to the much greater values of the dielectric constant, it was convenient to use a small spiral resonator having a resonant wave length of 0.4111 meter in air. Although this resonator had a relatively far larger stray field than the other it was so small that it could be used with about 120 cc. of solution in a double-walled Pyrex vessel jacketed with circulating water of the desired temperature.

In the case of all the solutions investigated the variation of dielectric constant with temperature can be expressed with an accuracy as great as that of the measurements by means of the second degree equation: $\epsilon = a - b(t - 25) + c(t - 25)^2$. In this equation ϵ denotes the dielectric constant at temperature t, a is the dielectric constant at 25°, and b and c are constants. The experimental results which follow are therefore presented in terms of these constants.

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(4) Wyman, *Phys. Rev.*, **35**, 623 (1930).

(5) Wyman and McMeekin, THIS JOURNAL, **55**, 915 (1933).

II. **Alcohol–Ether Mixtures.**—These solutions were made up gravimetrically from the best commercial materials. The density of the alcohol, determined with a pycnometer, was found to be 0.7853 as compared with the figure 0.7851 given by "International Critical Tables." The discrepancy would correspond to less than 0.07% H_2O, which would make a difference of about 0.03 in the dielectric constant, an amount not greater than the errors of the measurement. In the case of the ether, owing to the high vapor pressure, it was not practicable to determine the density so accurately. The figure obtained, 0.708, is to be compared with the value 0.7077 from "International Critical Tables." It seemed unwise to attempt further purification of the sodium distilled ether from a sealed metal container on which the measurements are based. The results are contained in Table I.

TABLE I

DIELECTRIC CONSTANT OF MIXTURES OF ETHANOL AND ETHER IN TERMS OF THE EQUATION: $\epsilon = a - b(t - 25) + c(t - 25)^2$

Ethanol, weight per cent.	ρ (25°)	a	b	$c \times 10^5$
0	0.708	4.235	0.0198	5
13.08	.722	5.885	.0323	18
20.86	.728	6.998	.0409	24
30.82	.737	8.712	.0540	31
41.24	.745	10.76	.0694	38
51.47	.752	12.89	.0858	42
61.93	.7614	15.26	.1018	45
70.05[a]	.7677	17.20	.1145	45
77.40	.7708	18.90	.1246	44
86.20	.7766	20.96	.1369	41
100.00	.7853	24.28	.1570	20

[a] Composition based on dielectric constant at 20°.

Urea Solutions.—The urea solutions were made up gravimetrically from Merck C. P. product and the density of each determined at 25° with a pycnometer. It was found that solutions allowed to stand for several hours at a temperature above 30 or 35° underwent a change associated with an increase of conductivity. For this reason measurements at lower temperatures were made first and the work above 25° was carried out as quickly as possible before the conductivity had shown any considerable increase, and before the dielectric constant showed any change independent of temperature. A similar change in the dielectric properties of urea solutions after standing for several days has been reported by Walden and Werner,[6] and Kockel[7] states that above 35° urea undergoes an irreversible change. The results are given in Table II and shown graphically in Fig. 1, where the full lines correspond to the values of *a*, *b* and *c* given in Table II and the circles are the experimental points. The accuracy of these data is not so great as in the case of the alcohol–ether mixtures owing to the far greater

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(6) Walden and Werner, *Z. physik. Chem.*, **129**, 405 (1927).

(7) Kockel, *Ann. Physik*, **77**, 417 (1925).

TABLE II

DIELECTRIC CONSTANT OF UREA-WATER MIXTURES IN TERMS OF THE EQUATION: $\epsilon = a - b(t - 25) + c(t - 25)^2$

Weight per cent. of urea	ρ 25°	Moles/liter (25°)	a	b	$c \times 10^6$
0	0.9971	0	78.54	0.362	70
11.52	1.0284	1.973	83.90	.376	75
20.31	1.0524	3.559	87.95	.385	81
29.64	1.0788	5.325	91.76	.391	85
36.83	1.0994	6.743	94.43	.394	89
42.47	1.1159	7.892	96.58	.397	92

conductivities which reduce the sharpness of the resonance settings. The conductivity of a 2.5 molar solution at 25° was about 37 × 10^{-6} ohms^{-1}.

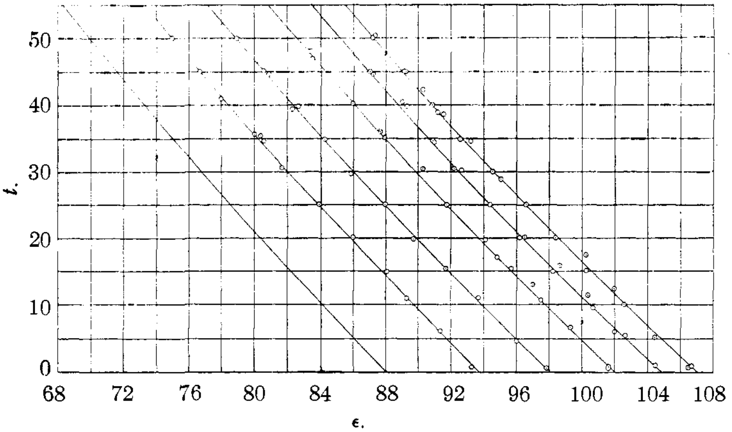

Fig. 1.

IV.—The data given in section II on the ethanol-ether mixtures may be compared with the results of other investigators. In the case of earlier

TABLE III

VALUES REPORTED FOR THE DIELECTRIC CONSTANT OF ETHER

Observer	Temperature, °C.	Dielectric constant
Richards and Shipley[8]	20	4.355
King and Patrick[9]	20	4.35
Grimm and Patrick[10]	34.5	4.11
Meyer[11]	16.6	4.3446
Scheremetzinskaja[12]	20	4.811
Estermann[13]	20	4.276
Matsouike[14]	25	4.362

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(8) T. W. Richards and J. W. Shipley, THIS JOURNAL, **41**, 2002 (1919).

(9) King and Patrick, *ibid.*, **43**, 1835 (1921).

(10) Grimm and Patrick, *ibid.*, **45**, 2794 (1923).

(11) E. H. L. Meyer, *Ann. Physik*, **75**, 801 (1924).

(12) S. Scheremetzinskaja, *J. Russ. Phys.-Chem. Soc., Phys. Teil.*, **59**, 499 (1927).

(13) Estermann, *Z. physik. Chem.*, **B1**, 134 (1928).

(14) Matsouike, *Proc. Imp. Acad. Tokyo*, **5**, 29 (1929).

data on pure ether, there is considerable disagreement, as shown by Table III. The author's value of 4.336 at 20° is in best agreement with the figures of Richards and Shipley and of King and Patrick. The latter observers also report the dielectric constant of mixtures of ethanol and ether of 10, 20, 30, 100% by weight at 20°. Their values, which are given only to either two or three significant figures, are 1 or 2% higher than those reported above.

As regards the urea solutions there is a considerable discrepancy between the measurements at a single temperature by Harrington,[15] Furth[16] Walden and Werner,[6] Kniekamp[17] and Devoto,[18] none of which were extended to a concentration greater than about 3 moles per liter. The present results, on the basis of the limiting value of the dielectric constant–concentration curve at zero concentration, agree best with the values of Walden and Werner.[6]

Kockel[7] has carried out an investigation of the effect of temperature on the dielectric constant of urea solutions of 5, 10 and 15% by weight. These results have been applied by Lange and Robinson[19] to their data on the integral heats of dilution of potassium chloride in 5% urea solutions on the basis of the theory of Debye. Lange and Robinson point out that in accordance with an extension of the original theory the limiting slope of the curve relating the heat to the square root of the molar concentration should be given approximately by the expression

$$\frac{-1.66116 \times 10^7}{\epsilon} \times \frac{1}{\sqrt{\epsilon T}}\left(1 + \frac{T}{\epsilon}\frac{d\epsilon}{dT}\right) = A$$

where ϵ is the dielectric constant of the solvent and T is the absolute temperature. In terms of Kockel's data this expression actually demands a negative heat of dilution ($A = -228$) for potassium chloride in 5% urea. This is quite at variance with the facts, which show that the heats in this solvent are positive (A observed $= 332$) and only slightly lower than those in water and in a 15% sugar solution, for which the theoretical values of A are given as 661 and 532 and the observed values as 376 and 386, respectively. On the basis of the data presented in this paper the value of A calculated from the above expression for the 5% urea solution is 440, which is in as good agreement with the facts as in either of the other cases. It may be noted that the theoretical values of A for water as well as the 15% sugar solution given by Lange and Robinson are also based on the data of Kockel. If Wyman's[4] data for water, used elsewhere by Lange, are substituted, the value obtained for A is 513.

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(15) Harrington, *Phys. Rev.*, **8**, 581 (1916).

(16) Furth. *Ann. Physik*, **70**, 163 (1923).

(17) Kniekamp, *Z. Physik*, **51**, 95 (1928).

(18) Devoto, *Gazz. chim. ital.*, **60**, 520 (1930).

(19) Lange and Robinson, THIS JOURNAL, **52**, 4218 (1930). The author's attention was called to these results by Professor George Scatchard.

Summary

A report is given of a study of the variation with temperature, between 0 and 50°, of the dielectric constant of ethanol–diethyl ether and urea–water solutions as determined by a resonance method at wave lengths between 3.6 and 20 meters. The results are compared with data of previous investigators, and, in the case of the urea–water solutions, are applied to studies of Lange and Robinson on heats of dilution.

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[CONTRIBUTION FROM THE WALKER LABORATORY OF RENSSELAER POLYTECHNIC INSTITUTE]

The Binary System Lead Iodide–Potassium Iodide[1]

BY HENRY S. VAN KLOOSTER AND EDWIN I. STEARNS

The melting point of lead iodide has been reported at such variant temperatures as 358[2] and 412°.[3] The melting point of potassium iodide has been given as low as 634° (1878)[4] and as high as 723°.[5] Many workers have confirmed the fact that only the double salt $KPbI_3 \cdot 2H_2O$ exists in the ternary system PbI_2–KI–H_2O,[6,7] but the anhydrous binary system has not heretofore been examined.

C. H. Herty[8] has driven off the water from this hydrate, $KPbI_3 \cdot 2H_2O$, and states that at 310° the salt decomposes with the liberation of iodine. It was therefore the purpose of this work to find the melting points of these two iodides and to decide what anhydrous double salts they form by determining the phase diagram by means of cooling curves.

The difficulty in melting lead iodide is that it decomposes in the presence of air. Several oxyiodides have been reported[9] but they have not been examined in the light of the phase rule and are thus to be considered on probation.

Apparatus and Materials.—The tube used to melt the various mixtures consisted, as illustrated in Fig. 1, of an outer test-tube and an inner air-excluding and thermocouple-protecting tube. This inner tube excluded the air by three factors. Its volume expelled nearly all the air to begin with, and further access of air was hindered both by the snugness with which the two tubes fit together and by the bulge of the inner tube resting upon the rim of the outer. The amount of decomposition could be seen by the iodine

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[1] A thesis presented in partial fulfilment of the requirements for the degree of Master of Science in the Graduate School of Arts and Science of Rensselaer Polytechnic Institute.

[2] F. Matthes and K. Monkemeyer, *Neues Jahrb. B. B.*, **22**, i (1906).

[3] German and Metz, *J. Phys. Chem.*, **35**, 1944 (1931).

[4] "Phys.-Chem. Tabellen," Landolt und Börnstein, 1894.

[5] J. McCrae, *Wied. Ann.*, **55**, 95 (1895).

[6] N. Demassieux, *Compt. rend.*, **177**, 51 (1923).

[7] L. J. Burrage, *J. Chem. Soc.*, **129**, 1703 (1926).

[8] Herty, *Amer. Chem. J.*, **18**, 292 (1896).

[9] Mellor, "Treatise," Vol. VII, p. 766.