

No.	Source of lead, locality	Geol. age		Isotope abundances			Mean mass number	Atomic weight	
		years $\times 10^{-6}$	204	206	207	208		Physical	Chemical
7	Galena I, Joplin, Mo.	230	1.000	21.65	15.88	40.8	207.203	207.178	207.22
8	Galena II, Joplin, Mo.	230	1.000	21.60	15.73	40.3	207.200	207.175	
			1.000	21.65	15.75	40.45	207.200	207.175	
9	Galena, Metalline Falls, Wash.	80	1.000	19.30	15.73	39.5	207.228	207.203	207.21
10	Cerussite, Wallace, Idaho	80	1.000	15.98	15.08	35.07	207.239	207.214	207.21
			1.000	16.10	15.13	35.45	207.242	207.217	
11	Wulfenite and vanadinite, Tucson Mts., Arizona	25	1.000	18.40	15.53	38.1	207.229	207.204	207.22
12	Galena, Saxony, Germany		1.000	17.34	15.47	37.45	207.240	207.215	
			1.000	17.38	15.44	37.3	207.238	207.213	

dances diverges appreciably from the International value 207.21 only in one case out of ten, that of lead from Joplin, Mo., U. S. A.

The value 207.21 is retained for the table, al-

though in the future it is apparent that the geological occurrence of common lead must be taken into account so far as its atomic weight is concerned.

[CONTRIBUTION FROM SOUTHWESTERN COLLEGE]

The Phenylthiourea-Ethanol and Urea-Methanol Systems and the Debye Salting-Out Theory¹

BY R. W. WRIGHT, LOVELL S. STUBER AND PENROSE S. ALBRIGHT

I. Introduction

P. Debye and co-workers developed a theory² to account for the salting-out effect in which he pointed out that the dielectric constant of the system to which salt is added should largely determine the extent to which the solute is salted-in or salted-out. If the dielectric constant of the system decreases with increasing concentration of the solute, salting-out is expected, and if it increases salting-in should occur. Albright and Williams^{3,4} have investigated the dielectric constants of several aqueous systems for which reliable salting-out data are available. The present paper deals with one non-aqueous system for which reliable salting-in data⁵ are available and one non-aqueous system for which, so far as the authors know, no such data are available. The latter system should lend itself readily to a study of its salting-in or salting-out characteristics.

II. Purification of Materials

(a) **Ethanol.**—Commercial absolute ethanol from the U. S. Industrial Chemical Co. was distilled from concentrated sulfuric acid (15 cc. of sulfuric acid per liter of alcohol), then from alkaline silver nitrate (5 g. per liter), refluxed with freshly prepared lime,⁶ then with magnesium

ethylate. The magnesium ethylate was prepared by refluxing 5 g. of magnesium, 60 cc. of alcohol (from the lime distillation) and 0.5 g. of iodine; 900 cc. of the lime distillate was then added and the mixture refluxed for one hour after which the final distillation was made.⁷ The ethanol so prepared had a boiling point of 78.2° corrected to 760 mm. and a density of 0.78515 \pm 0.00002 at 25.00° which compares with 0.78506 given by the "International Critical Tables."

(b) **Methanol.**—The methanol was purified exactly as was the ethanol. As thus prepared it had a density at 25.00° of 0.78666 \pm 0.00002 which compares with 0.78661 given by the "International Critical Tables."

(c) **Phenylthiourea.**—Phenylthiourea purchased from the Eastman Kodak Company was recrystallized several times from ethanol prepared as described. The melting point was 151.6–152.0°.

(d) **Urea.**—The urea was a product of the General Chemical Co. and was labeled "pure." It was four times fractionally crystallized from progressively better methanol. The melting point of this purified material was the same as that given by the "International Critical Tables," 131.7°.

III. Apparatus

The apparatus employed in the measurement of dielectric constants was a bridge using a frequency of 570,000 cycles per second and employing the substitution principle. It was described in a paper by Albright.⁴

A modified form of the Ostwald pycnometer was used to determine densities.

IV. Experimental Data

In making up solutions, carefully dried solute was weighed, then solvent added and the solution thus formed weighed. Precautions were taken to prevent contamination by atmospheric moisture. Densities were computed *in vacuo*.

(7) Lund and Bjerrum, *Ber.*, **64B**, 210 (1931).

(1) A more detailed account may be found in theses by Mr. Wright and by Mr. Stuber in the Southwestern College Library, Winfield, Kansas. Mr. Wright's thesis deals with the first-mentioned system, Mr. Stuber's with the second.

(2) (a) Debye and McAulay, *Physik. Z.*, **26**, 22 (1925); (b) Debye, *Z. Physik. Chem.*, **130**, 56 (1927).

(3) Albright and Williams, *Trans. Faraday Soc.*, **33**, 247 (1937).

(4) Albright, *THIS JOURNAL*, **59**, 2098 (1937).

(5) Thorin, *Z. Physik. Chem.*, **89**, 689 (1915).

(6) Scholl, Hutchison and Chandlee, *THIS JOURNAL*, **57**, 2542 (1935).

(a) The Phenylthiourea-Ethanol System.

The data taken are shown in tabular form in Table I. The 3.566% solution displayed less conductivity than the previous two, consequently the bridge was more sensitive; whence the authors give its dielectric constant measurement more weight than those of the previous two measurements.

If we let D represent the dielectric constant, d^{25}_4 the density, and p the weight per cent. phenylthiourea, that part of the data taken at 25.00° may be expressed by the following two empirical equations

$$D = 24.37 + 0.084p$$

$$d^{25}_4 = 0.78515 + 0.00344p$$

TABLE I

THE PHENYLTHIOUREA-ETHANOL SYSTEM

Wt. % phenylthiourea	Temp., °C.	Dielectric constant		Density	
		Exptl.	From eq.	Exptl.	From eq.
0.000	25.00	24.37 ^a	24.37	0.78515	0.78515
1.005	25.00	24.50	24.45	.78938	.78861
2.006	25.00	24.55	24.54	.79208	.79205
2.821	25.00	24.50	24.61	.79500	.79485
3.037	25.00	24.43	24.63	.79560	.79560
3.566	25.00	24.70	24.67	.79755	.79742
0.000	28.00	23.9278527

Thorin's salting-in data were taken at 28.00°. The authors preferred to obtain dielectric constant and density data at 25.00° and pure ethanol at 28.00 and assume the 28.00° curves parallel to the 25.00° curves up to the approximately 4% saturation value.

(b) The Urea-Methanol System.—The data taken are shown in tabular form in Table II. The concentration of a saturated solution was determined by dissolving an excess of urea in methanol by heating above 25°, then placing the solution in a 25.00° constant temperature bath after which the containing flask was shaken frequently while the excess urea crystallized out; 4.7069 g. of the clear liquid was then withdrawn and weighed after which drying was carried out under a partial vacuum and gentle heating. The residual urea weighed 0.9270 g. giving a concentration of closely 19.7 weight per cent. urea for a saturated solution.

If we let D , d^{25}_4 and p represent the dielectric constant, density and weight per cent. urea, respectively, at 25.00° of the urea-methanol system then our data may be closely expressed by the two empirical equations

$$D = 32.74 + 0.578p - 3.2 \times 10^{-3}p^2$$

$$d^{25}_4 = 0.78666 + 4.062 \times 10^{-3}p + 7.3 \times 10^{-6}p^2$$

TABLE II

THE UREA-METHANOL SYSTEM AT 25.00°

Wt. % urea	Dielectric constant		Density	
	Exptl.	From eq.	Exptl.	From eq.
0.000	32.74	32.74	0.78666	0.78666
1.999	33.86	33.89	.79480	.79481
4.058	35.16	35.04	.80328	.80325
6.030	36.20	36.10	.81140	.81142
8.834	37.41	37.59	.82322	.82311
10.14	38.26	38.27	.82848	.82860
15.40	40.84	40.88	.85106	.85095
18.92	42.55	42.54	.86602	.86613
19.7 ^a	...	42.8986951

^a Saturated solution.

V. Discussion

Thorin's salting-in data for the phenylthiourea-ethanol system at 28.00° are shown graphically in Fig. 1. As these data show, salting-in occurred for all salts upon which he reported.

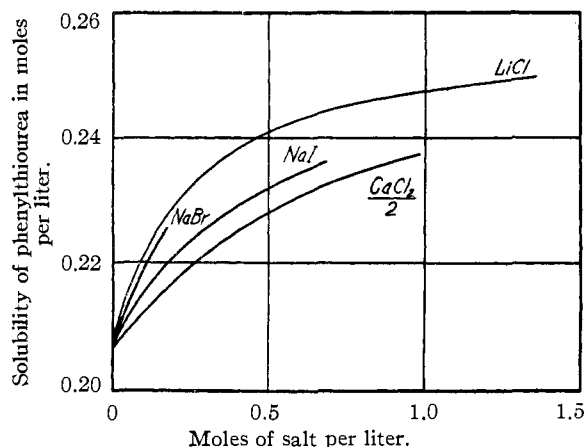


Fig. 1.—Thorin's salting-in data for the phenylthiourea-ethanol system shown graphically.

An application of Debye's theory calls definitely for a salting-in rather than a salting-out because the slope of the dielectric constant curve is positive. However, a quantitative application of his theory is not justified for the reason that it would have to be based upon the uncertain extrapolation of the dielectric constant curve to 100% phenylthiourea based upon the first 3.566%.

There is one other thing, however, worth noting. Of the three 1-1 valence type salts upon which Thorin reported, the smaller the ions the more salting-in occurred. According to the Debye theory salting-in is largely due to the excessive accumulation of the dissolved non-electrolyte in the immediate vicinity of the ions. The smaller the ions, the more there would be of the critical

(8) This compares with 24.28 found by Wyman, THIS JOURNAL, 55, 4116 (1933).

room close to the average position of the charges upon the ions into which salting-in could occur. This may be the reason for the order just noted.

The rapid rise of the dielectric constant of the urea-methanol system, with increased percentage of urea, should cause a very marked salting-in effect when salts are added to this system. The authors hope that with the data presented here available, some workers interested in measuring the salting-in or salting-out effect will be encouraged to work with this system and thus test Debye's theory with another non-aqueous system, and one in which prediction has come first and test followed the prediction.

VI. Summary

Dielectric constant and density measurements have been made on the phenylthiourea-ethanol system at 25.00°, and on ethanol at 28.00°. The salting-in characteristics of this non-aqueous system were found to be at least in qualitative agreement with Debye's salting-out theory.

Dielectric constant, density and saturation data are given for the urea-methanol system at 25.00°. The dielectric constant rises rapidly with increasing concentration of urea, leading to the prediction that if salts are added to the system urea will be strongly salted-in.

WINFIELD, KANSAS

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES DIVISION, GENERAL MOTORS CORPORATION]

The Vapor Phase Catalytic Conversion of Tertiary Butylmethylcarbinol and Tertiary Butylethylene

BY PAUL L. CRAMER AND A. L. GLASEBROOK

In the syntheses in this Laboratory of certain isomeric hexenes a search was made for a more convenient method for dehydrating *t*-butylmethylcarbinol. Previous methods,¹ in which acid catalysts and liquid phase reactions were employed, did not appear to be altogether suitable for the dehydration of large amounts of the alcohol. Preliminary experiments on the vapor phase dehydration of *t*-butylmethylcarbinol over activated alumina gave surprisingly different results from those obtained by previous methods. *t*-Butylethylene was found to be the principal olefin formed over activated alumina, whereas previous methods gave only negligible amounts of the normally expected olefin. The liquid phase dehydration of the alcohol with acid catalysts¹ gave the rearranged products, tetramethylethylene and unsym-methylisopropylethylene. These somewhat anomalous results suggested a more detailed study of the vapor phase reactions of both *t*-butylmethylcarbinol and *t*-butylethylene over activated alumina, and also over an acid catalyst, anhydrous aluminum sulfate. Furthermore, a method for the preparation of *t*-butylethylene by the direct dehydration of *t*-butylmethylcarbinol rather than by the thermal decomposition of the

acetate^{1,2} or the methyl xanthate³ of the alcohol was desirable.

An outline of the above experiments together with the analyses of the resulting olefins is presented in Table I.

The order in which the above three olefins are formed by the dehydration of *t*-butylmethylcarbinol by previous procedures¹ is inverted by the vapor phase dehydration of the alcohol over activated alumina. *t*-Butylethylene is formed in yields as high as 64% by volume. The reaction is largely independent of the reaction temperature. Attempts to dehydrate the alcohol over alumina by the static liquid phase method were unsuccessful.

In accord with the results obtained by previous liquid phase procedures with acid catalysts,¹ the vapor phase dehydration of the *t*-butylmethylcarbinol over anhydrous aluminum sulfate gives the rearranged olefins, tetramethylethylene and unsym-methylisopropylethylene. Negligible amounts of the normally expected olefin, *t*-butylethylene, are formed.

t-Butylethylene was passed unchanged over activated alumina, whereas, over anhydrous aluminum sulfate, *t*-butylethylene is rearranged to give

(1) For complete references see Whitmore and Rothrock, *THIS JOURNAL*, **55**, 1106 (1933); Whitmore and Meunier, *ibid.*, **55**, 3721 (1933).

(2) Cramer and Mulligan, *ibid.*, **58**, 373 (1936).

(3) Fomin and Sochanski, *Ber.*, **46**, 246 (1913); Schurman and Boord, *THIS JOURNAL*, **55**, 4930 (1933).