

0.0914, is added to our E_0 , 0.2441, we get, as E_0 for the tenth-normal electrode, 0.3355, in fair agreement with MacInnes.

Summary

Measurements of electromotive force were made at 25° using the cell: H₂, buffer solution, KCl (satd.), HgCl, Hg. By extrapolation of the data obtained with acetate, phosphate, borate and glycolate buffer solutions, a single value of E_0 for this calomel half cell was obtained, on the basis of the thermodynamic dissociation constants of the acids used. The same value was

obtained from measurements with hydrochloric acid in sodium chloride solutions, but not with the acid alone nor with potassium chloride. This E_0 value was used to assign pH values to a series of standard solutions from pH 1 to 9, without correction for liquid junction potentials. It is suggested that this pH scale may be used as a basis for the exact determination of the thermodynamic dissociation constants of weak acids from hydrogen electrode measurements with buffer solutions, containing the acid and its sodium salt, provided that the pK of the acid lies between 4 and 9.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Apparent Molal Volume of Inorganic Salts in Methanol Solution¹

BY J. B. STARK AND E. C. GILBERT

Since the work of Masson² showing that the apparent solution volume of a large number of salts in aqueous solution is a linear function of the square root of the volume concentration, considerable interest has been attached to the problem and it has been studied extensively in numerous laboratories.³

Redlich and Rosenfeld⁴ have attempted to justify this behavior on the basis of the Debye-Hückel theory, although the linear relationship where observed often seems to hold in solutions far too concentrated for such treatment. Johnson and Martens⁵ found the relationship to hold for alkali halides in liquid ammonia. However, as the number of substances investigated has increased and the experimental precision has improved, it is becoming more evident that the rectilinear relationship is by no means universally valid.

Deviations from relationships which are based on interionic attraction frequently are more pronounced in solvents of low dielectric or become evident at lower concentration, hence it was be-

lieved that a study of the apparent molal volume of salts in alcoholic solution might provide useful information, particularly if salts were chosen for which data are also available for their aqueous solutions. Methanol was chosen as the solvent for this study because of its higher solvent power for salts and its relative ease of purification. Density data in the literature for alcoholic solutions of inorganic salts are for the most part somewhat unsatisfactory and few calculations of the apparent molal volume have been made. Vosburgh, Connell, and Butler⁶ studied the electrostriction produced by alkali halides in aliphatic alcohols and calculated apparent molal volumes. Gibson and Kincaid³ have recently reported the apparent volumes, also of alkali halides, in methanol and glycol. The data of Jones and Fornwalt⁸ obtained for viscosity measurements, also permit easy and accurate calculation of the apparent molal volumes of alkali and ammonium halides.

Experimental

Ammonium nitrate, potassium thiocyanate, calcium nitrate, and mercuric chloride were chosen as suitable salts, and the densities of a series of solutions of varying concentrations were determined at 25°, using methanol as solvent.

Materials.—Synthetic methanol was purified by the method of Lund and Bjerrum,⁷ omitting the treatment with tribromobenzoic acid from their procedure. The density of the alcohol obtained was 0.786644. The

(1) This paper is taken from a thesis presented by J. B. Stark in partial fulfillment of the requirements for the M.S. degree at the Oregon State College, June, 1937.

(2) Masson, *Phil. Mag.*, [7] **8**, 218 (1929).

(3) Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931); Scott, *J. Phys. Chem.*, **35**, 2315 (1931); Gucker, *Chem. Rev.*, **13**, 111 (1933); *J. Phys. Chem.*, **38**, 307 (1934); Scott and Bridger, *ibid.*, **39**, 1035 (1935); Pesce, *Gazz. chim. ital.*, **65**, 448 (1935); Kruis, *Z. physik. Chem.*, **B34**, 1 (1936); Gibson and Kincaid, *THIS JOURNAL*, **59**, 25, 579 (1937); and others.

(4) Redlich and Rosenfeld, *Z. physik. Chem.*, **A155**, 65 (1931).

(5) Johnson and Martens, *THIS JOURNAL*, **58**, 15 (1936).

(6) Vosburgh, Connell, and Butler, *J. Chem. Soc.*, 933 (1933).

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

density given for methanol in the "I. C. T." is 0.78660 and that recently found by Jones and Fornwalt⁸ is slightly lower, 0.786545. If this difference in density is caused by water it indicates an approximate maximum of 0.03% present in the alcohol used.

The salts used were of the highest purity obtainable, and were further purified (except calcium nitrate) by three crystallizations from ethyl alcohol. Following this treatment: Potassium thiocyanate was purified and dried by the method of Kolthoff and Lingane.⁹ Ammonium nitrate was dried in a vacuum oven at 70° and then over phosphorus pentoxide. Mercuric chloride was dried only over phosphorus pentoxide. Calcium nitrate was dried over phosphorus pentoxide and then heated in an oven for four hours at 150°.

Manipulation—The pycnometer (25-ml.) was designed to minimize evaporation losses and consisted of a thin glass bulb with a capillary neck upon which was a line for calibration. Above the capillary neck was a small thistle top which was fitted with a ground stopper. Solutions were introduced, by pressure of dry air, through a fine capillary. Duplicate settings of the meniscus were always made and the weighings for these seldom failed to agree within ± 0.1 – 0.2 mg.

TABLE I

EXPERIMENTAL DETERMINATION OF APPARENT MOLAL VOLUMES OF SALTS IN METHANOL

C, moles/l.	C ^{1/2}	Density	ϕ_v , ml.
KCNS			
0.1811	0.426	0.79964	32.23
.3438	.586	.80187	33.92
.3918	.626	.81419	34.15
.8307	.911	.84327	36.87
.9545	.977	.85141	37.265
1.4999	1.225	.88537	39.87
NH ₄ NO ₃			
0.2518	0.502	0.79959	36.40
.4679	.684	.81011	37.99
.7763	.881	.82468	39.47
.8325	.912	.82730	39.67
.9080	.951	.83083	39.89
HgCl ₂			
0.1092	0.331	0.81264	42.60
.2713	.521	.85120	42.69
.3537	.595	.87070	42.62
.6931	.833	.95145	42.89
.8493	.922	.98862	42.83
Ca(NO ₃) ₂			
0.1705	0.413	0.81113	26.06
.3215	.567	.83230	28.06
.5344	.731	.86163	30.22
.5439	.739	.88281	30.58
.7487	.865	.98063	32.02
1.086	1.042	.93528	34.67
1.175	1.08	.94724	34.82
1.583	1.25	.99674	37.69
2.025	1.42	1.05430	39.71
2.045	1.43	1.05755	40.19

(8) Jones and Fornwalt, *THIS JOURNAL*, **57**, 2041 (1935).

(9) Kolthoff and Lingane, *ibid.*, **57**, 2126 (1935).

Each solution was made up separately by weight to avoid cumulative errors. All weights were reduced to vacuum. The temperature of the constant temperature bath was adjusted to $25 \pm 0.02^\circ$ with a thermometer which had been calibrated by the Bureau of Standards, and fluctuations were noted on a Beckmann thermometer.

Results

The results of the density determinations are shown in Table I, together with the values of the apparent molal volumes calculated from them by the equation

$$\phi_v = [V(d_1 - d_2) + g]/n_2d_1$$

where V is volume of solution; d_1 , density of solvent; d_2 , density of solution; g , grams of solute; and n_2 , moles of solute.

Apparent molal volumes are plotted against $C^{1/2}$ (C is concentration in moles per liter) in Fig. 1. Included also in the graph are curves for potassium iodide and bromide constructed from the very accurate density data of Jones and Fornwalt⁸ in a concentration range lower than that attained in the present work.

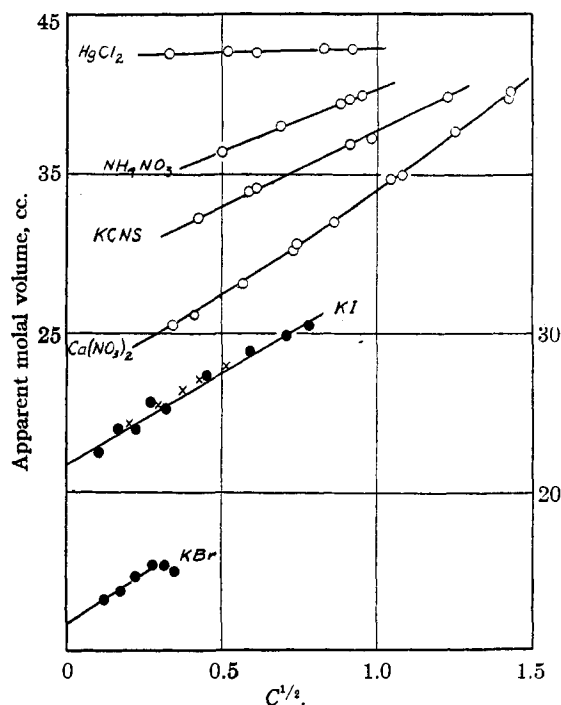


Fig. 1.—Apparent molal volume of salts in methanol. Solid circles, data of Jones and Fornwalt;⁸ crosses, data of Vosburgh, Connell, and Butler.⁹

Inspection of the curves and comparison with those for the same salts in aqueous solution (not shown in this paper) justify the conclusion that the same type of behavior is in general common to both solvents. There are some differences which

may be explained in terms of solvent properties. In all cases the slope in alcoholic solution is greater than in water, and the slope for the higher valence types except mercuric chloride is greater than for the simpler type. The values at infinite dilution in methanol are considerably less than in water. This general result has been justified by Vosburgh, Connell, and Butler⁶ in their work on electrostriction. There is also a greater individual variation in this value among the salts in methanol than in water. For the four salts KI-KCNS-NH₄NO₃-Ca(NO₃)₂ in aqueous solution ϕ_v extrapolated is, respectively, 45.2-48.0-47.5-43.3, while in methanol for the same series ϕ_v is 21.9-28.2-32.6-21.0. Other differences are not interpreted so easily. The behavior of mercuric chloride is anomalous, the slope being practically zero.

Calcium nitrate in methanol shows considerably less curvature than in water. Disregarding the last point in dilute solution the curve might be drawn as a straight line. In methanol the curve for ammonium nitrate is straight within the limit

of error. Gucker^{3b} has shown likewise that the curve is almost linear in water solutions. The curve for potassium iodide from the results of Jones and Fornwalt shows good agreement with that of Vosburgh, Connell, and Butler. Potassium thiocyanate gives a straight line in both solvents. In addition it might be mentioned by way of completeness that the data of Jones and Fornwalt for ammonium chloride likewise yield a linear curve, although it is not shown in the figure.

Summary

1. The densities of methanol solutions of potassium thiocyanate, ammonium nitrate, calcium nitrate, and mercuric chloride have been determined for several concentrations of each salt at 25°.

2. Apparent molal volumes have been calculated for these and other salts in methanol, and the results presented graphically.

3. The curves are discussed and compared with those for the same salts in aqueous solution.

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The Preparation of Pure *d*-Riboflavin from Natural Sources

BY R. D. GREENE AND A. BLACK

The preparation of *d*-riboflavin from natural sources has been described by a number of investigators¹⁻⁹ and more recently Karrer¹⁰ and Kuhn¹¹ have reported the synthesis. Considerable differences in the biological activities of the preparations from different laboratories have suggested that probably there were variations in the degree of purity of the natural product. It has been our experience, which has been gained from work extending over three and a half years, that it is not a simple matter to make pure riboflavin. In our early work in 1935, we prepared a

lot of material by following the methods of Kuhn² and Karrer,³ which consisted of adsorption on fuller's earth, elution with pyridine-alcohol-water solutions, repeated reabsorptions on lead sulfide and elutions with boiling water followed by precipitations. The resulting crystals appeared to be pure and more recent tests have confirmed this. Although the yields were fair, the method was rather complicated and tedious. Consequently we have endeavored to improve it and have developed a method which is based upon adsorptions on fuller's earth and the use of immiscible solvents.

Adsorption of Riboflavin.—In the concentration of riboflavin from the crude extracts of natural products adsorption steps have been used invariably by other investigators. Of the adsorbents commonly used we have tried fuller's earth, frankonite and charcoal. Charcoal seems to have the greatest adsorptive power, but removal of the riboflavin is difficult. The behavior of fuller's earth and frankonite in adsorption and subsequent removal of riboflavin is very similar. As a first step in concentration,

- (1) Ellinger and Koschura, *Ber.*, **66**, 315 (1933).
- (2) Kuhn, György and Wagner-Jauregg, *ibid.*, **66**, 317, 576 (1933).
- (3) Karrer and Schöpp, *Helv. Chim. Acta*, **17**, 735 (1934).
- (4) Booher, *J. Biol. Chem.*, **102**, 39 (1933); **107**, 591 (1934).
- (5) Lepkovsky, Popper and Evans, *ibid.*, **108**, 257; *ibid.*, **109**, Proc. 54 (1935).
- (6) Itter, Orent and McCollum, *ibid.*, **108**, 579 (1935).
- (7) Elvehjem and Koehn, *ibid.*, **108**, 709 (1935).
- (8) Stare, *ibid.*, **111**, 567 (1935).
- (9) Ansbacher, Supplee and Bender, *J. Nutrition*, **11**, 401 (1936).
- (10) Karrer, Schöpp and Benz, *Helv. Chim. Acta*, **18**, 426 (1935).
- (11) Kuhn, Reinemund, Weygand and Ströbele, *Ber.*, **68**, 1765 (1935).