Studies on the Liquid-Liquid Partition Systems. II. The Determination of Water Activity by the Solvent Extraction Technique

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In the course of our study on the liquid-liquid partition systems, we desired to find a way to ascertain the water activity of various electrolyte solutions easily.

As Robinson and Stokes[1] have stated, the vapour pressure method is very accurate; the limit of the error is usually less than 0.01%. However, the method is not always easy to carry out because special apparatus must be prepared and a careful control of the experimental conditions is indispensable.

It seems that the water activity in an aqueous solution can be determined by the solvent extraction technique without any special difficulty, because the water content in an organic solvent in equilibrium with the solution can be measured by Karl Fischer titration, and it will be proportional to the water activity in the solution.

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1) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London (1959).

Högfeldt and his co-workers[2] have studied the extraction of water and acids from various acid solutions into organic solvents by Karl Fischer titration. In these systems, the water in the organic phase consists of two fractions, the free water and the hydrated water. They calculated the hydrated water content from the difference between the total water content as determined by Karl Fischer titration and the free water content as calculated from the water activity cited in the literature.

The present work was carried out to ascertain the accuracy of the value of the water activity determined by the solvent extraction method. For this purpose, benzene was equilibrated with various electrolyte solutions, and the concentration of water in the benzene phase was determined by Karl Fischer titration. Then the water activity of the solution was calculated.

The results were compared with the data in the literature, which had been determined by the vapor-pressure method.

Statistical Treatment

Symbols.

$\{H_2O\}$　　water activity
$[H_2O]$　　water concentration
γ　　　　activity coefficient

The following subscripts denote the activity, concentration or activity coefficient of water in:

"*aq*"　an aqueous phase
"*org*"　an organic phase
"*0*"　pure water, or an organic phase in equilibrium with pure water
"*n*"　an electrolyte solution, or an organic phase in equilibrium with the aqueous phase

When an aqueous solution is in equilibrium with an immiscible organic solvent, the distribution constant of water is defined as:

$$H_2O_{(aq)} \rightleftharpoons H_2O_{(org)} \quad (1)$$

$$K = \{H_2O\}_{org}/\{H_2O\}_{aq} \quad (2)$$

Moreover, an equation can be introduced for the ratio of the water activity in the organic phase in equilibrium with an electrolyte solution and pure water as:

$$\{H_2O\}_{aq,n}/\{H_2O\}_{aq,0} = \{H_2O\}_{org,n}/\{H_2O\}_{org,0} \quad (3)$$

When the water activity in pure water is defined as unity, Eq. 3 can be described, using the activity coefficient as:

$$\{H_2O\}_{aq,n} = \gamma_{org,n}[H_2O]_{org,n}/\gamma_{org,0}[H_2O]_{org,0} \quad (4)$$

Here the following will be assumed.

(i) The activity coefficient of water in the organic phase is constant when the water concentration in it is low.

(ii) The distribution of a small amount of the organic solvent in the aqueous phase does not change the character of the solution.

(iii) No extraction of species which carries water as hydrated water occurs.

On the basis of the first assumption $\gamma_{org,n}$ is equal to $\gamma_{org,0}$ and the water activity in the aqueous solution can be calculated as:

$$\{H_2O\}_{aq,n} = [H_2O]_{org,n}/[H_2O]_{org,0} \quad (5)$$

Thus the water activity of a certain solution can be determined from the ratio of the water concentration in two organic phases if these three assumptions can be made.

Experimental

Materials.—The following chemicals (of a specially-purified grade) were employed without further purification: benzene, potassium bichromate, potassium nitrate, potassium chloride, sodium chloride, strontium chloride, magnesium nitrate, and magnesium chloride. Solutions for Karl Fischer titration were obtained from the Mitsubishi Kasei Co. The sodium chloride was dried in an air-bath at 120°C for several hours and then stored in a desiccator. Sodium chloride solutions of various concentrations were prepared by weighing the dried sodium chloride. Saturated-salt stock solutions were prepared from the metal salts.

Procedures.—All of the procedures were carried out in a thermostated room at 25 ± 0.3°C. Twelve milliliters of benzene and 5 ml. of the sample solution were placed in glass-stoppered tubes (volume, 20 ml.). For the experiments with saturated solutions, 0.3—0.5 g. of the salt crystals was added to the sample solution in order to ensure saturation. A mechanical rotator (20 r. p. m.) was used for the agitation of the two phases in the tube; this rotation was continued overnight. It was confirmed by preliminary experiments that the distribution equilibrium was reached within one hour by this rotation. Then the two phases were centrifuged about 5 min. at 2000 r. p. m. This seems to be enough for the separation, because a centrifugation for over 15 min. at 3500 r. p. m. gave the same results.

Ten milliliters of the benzene were then pipetted out and the water content was titrated with a Karl Fischer apparatus (Kyoto Denshi Kogyo Co.).

Blank titration was carried out, and a small correction was made for the water coming from the air.

Results

The results are given in the following tables.

2) E. Högfeldt and B. Bolander, "Arkiv for Kemie," Band 21, nr 16, Almqvist & Wiksell, Stockholm (1963).

TABLE I.   THE WATER CONCENTRATION IN THE
BENZENE PHASE IN AN EQUILIBRIUM WITH
PURE WATER

Reference	Water concn., mol./l.
This work	0.034*
Högfeldt, Bolander[2]	0.032
Clifford[3]	0.026
Groschuff[4]	0.033
Hill[5]	0.035
Joris, Taylor[6]	0.025
Rosenbaum, Walton[7]	0.024
Stavely et al.[8]	0.033

* The average of the results.   The original
data are as follows :

0.0342	0.0340	0.0340	0.0342	0.0342	0.0339
0.0339	0.0342	0.0342	0.0342	0.0340	0.0340
0.0341	0.0342				

TABLE II.   WATER ACTIVITY IN VARIOUS
SATURATED SALT SOLUTIONS

Salt	$\{H_2O\}_{aq}$ Determined	Average	$\{H_2O\}_{aq}$ From Ref. 1
$K_2Cr_2O_7$	0.976 0.980 0.976	0.97_7	0.980
KNO_3	0.941 0.937 0.942	0.94_0	0.925
KCl	0.854 0.857 0.850	0.85_4	0.843
$NaCl$	0.756 0.757 0.762	0.75_8	0.753
$SrCl_2$	0.693 0.707 0.697	0.69_9	0.708
$Mg(NO_3)_2$	0.529 0.536 0.530	0.53_2	0.529
$MgCl_2$	0.326 0.326 0.320	0.32_4	0.330

TABLE III.   WATER ACTIVITY IN SODIUM
CHLORIDE SOLUTION

Concn. of NaCl (molality)	$\{H_2O\}_{aq}$ Determined	Average	$\{H_2O\}_{aq}$ From Ref. 1
0.50	0.984 0.983 0.985	0.98_4	0.984
1.0	0.970 0.967 0.970	0.96_9	0.967
2.0	0.931 0.938 0.931	0.93_3	0.932
3.0	0.889 0.892 0.908	0.89_6	0.893
4.0	0.855 0.856 0.854	0.85_5	0.852
5.0	0.812 0.815 0.814	0.81_3	0.807

Discussion

In these systems, the water concentration in
benzene is very low (maximum : 0.034 M water
per liter of benzene), and the benzene con-
centration in the aqueous phase is also very
low (maximum : 0.01 M benzene per liter of
water).   Thus, the first and second assumptions
seem to be established in the present systems.
From the results in the tables, we may also

conclude that the present method is accurate
to less than 1% when the procedures are car-
ried out properly.   The error of Karl Fischer
titration may be 0.1—0.5% at most.

By the use of this method, the water activity
of several electrolyte solutions can be determin-
ed.

Recommended Procedures

On the basis of the present results, the fol-
lowing procedures can be recommended :

Organic Solvents.—Benzene seems to be a
suitable solvent for this purpose.   If the sol-
vent is not very pure, it should be washed
several times with distilled water in order to
back-extract hydrophilic impurities.

Procedures.—Twelve to fifteen milliliters of
benzene and a few milliliters of the sample
solutions are placed in glass-stoppered tubes.
They are agitated until the distribution equilib-
rium is reached, and then centrifuged.   Ten
milliliters of benzene is pipetted out, and the
water content is titrated with a Karl Fishcer
solution 1 ml. of which is equivalent to about
1 mg. of water.

The following would be useful suggestions
for the experiments :

i)   The phase separation should be made
completely.   The present experiment showed
that a centrifugation at 2000 r. p. m. for 5 min.
is enough for the phase separation if the
viscosity of the solution is not high.

ii)   The solubility of water in an organic
phase is sometimes very sensitive to impurities ;
the blank test to determine the $[H_2O]_{org,0}$ in
Eq. 5 should be made.

iii)   The extraction of chemical species
which co-extract water as the hydrated water
should be checked.   The extraction of such
species increases the apparent water activity
determined by this method.   The extraction
of chemical species which may react with the
Karl Fischer reagent should also be checked.

iv)   Chemical species which will change
the mutual solubility should be avoided.   The
change in the mutual solubility may influence
the distribution of water (cf. assumptions i
and ii).

v)   The mutual solubility between an organic
solvent and an aqueous solution should not
be very high, for the high solubulity changes
the properties of each solution.

Summary

An attempt has been made to apply the
solvent extraction technique to the determina-
tion of the water activity in various electrolyte
solutions.

    3)   C. W. Clifford. *Ind. Eng. Chem.*, **13**, 631 (1921).
    4)   E. Z. Groschuff, *Elektrochemie*, **17**, 348 (1911).
    5)   A. E. Hill, *J. Am. Chem. Soc.*, **45**, 1143 (1923).
    6)   G. G. Joris and H. S. Taylor, *J. Chem. Phys.*, **16**, 45 (1948).
    7)   C. K. Rosenbaum and J. H. Walton, *J. Am. Chem. Soc.*, **52**, 3568 (1930).
    8)   L. A. K. Staverly and J. A. E. Moy, *Trans. Faraday Soc.*, **39**, 5 (1943).

Benzene was agitated with a sample solution until the distribution equilibrium was attained, the water content in the benzene was then measured by Karl Fischer titration. The water activity was calculated on the basis of the water content.

The results agree with the data obtained by the vapor pressure method. On the basis of these, a solvent extraction procedure has been recommended as an easy and rapid method to determine the water activity in various electrolyte solutions.

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