A SIMPLE, QUICK, AND PRECISE PROCEDURE FOR THE DETERMINATION OF WATER IN ORGANIC SOLVENTS

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ABSTRACT

A procedure for the UV/VIS-spectroscopic determination of water by the use of a solvatochromic pyridiniumphenolate betaine is given. The water content of organic solvents is calculated by a two parameter equation from λ_{max} of the dye. A typical detection limit is of the order of 1 mg in 1 ml solvent for rou-

tine spectrometers. The parameters for the determina-
tion of water are given for a number of commonly used
solvents.

INTRODUCTION

The residual water content of dried solvents is
important for preparative chemistry and may determine
yields, reaction products and selectivities. There is
no problem for solvents like ether which are commonly
stored over alkali metals; however a great number of
very hygroscopic solvents such as dimethyl sulfoxide,
dimethylformamide, or ethanol have to be stored neat
or over molecular sieves. Generally for preparative
work the water content of these solvents is unknown,
especially when the samples are old. The Karl-Fischer
titration[1] is a useful method for the determination of
water, but the titration needs special equipment
(dead-stop method) and "know how". Further complica-
tions occur in the presence of redox systems. So this
titration is not carried out as a standard procedure
in preparative work. A simple and uncomplicated method
for the determination of water has to be developped.
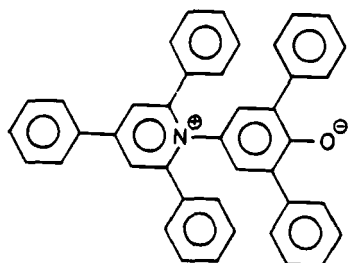
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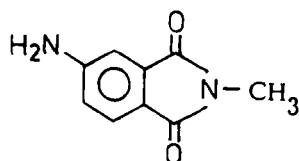
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$$E_T(30) = 28590 \ [kcal \cdot mol^{-1}]/\lambda_{max} \qquad (1)$$

Water determinations can be done using the fact that water has a very high solvent polarity compared with most solvents. So even small amounts of water can markedly increase the polarity of a solvent and this can be determined by a sensitive solvent polarity probe. Dimroth and Reichardt[2] used for the determination of water the peak shift of the pyridiniumphenolate betaine dye **1**,[3-5] which is very sensitive to the water content of a solvent sample. Dye **1** is the basis for the $E_T(30)$ polarity scale calculated with equation (1). The absorption wavelength of **1** is shifted from the short wavelength visible region in water (yellow solution) through the visible spectrum to the long wavelength region in acetone (green solution) up to the near infrared in solvents with low polarity like 1,4-dioxane. However the relation between the peak
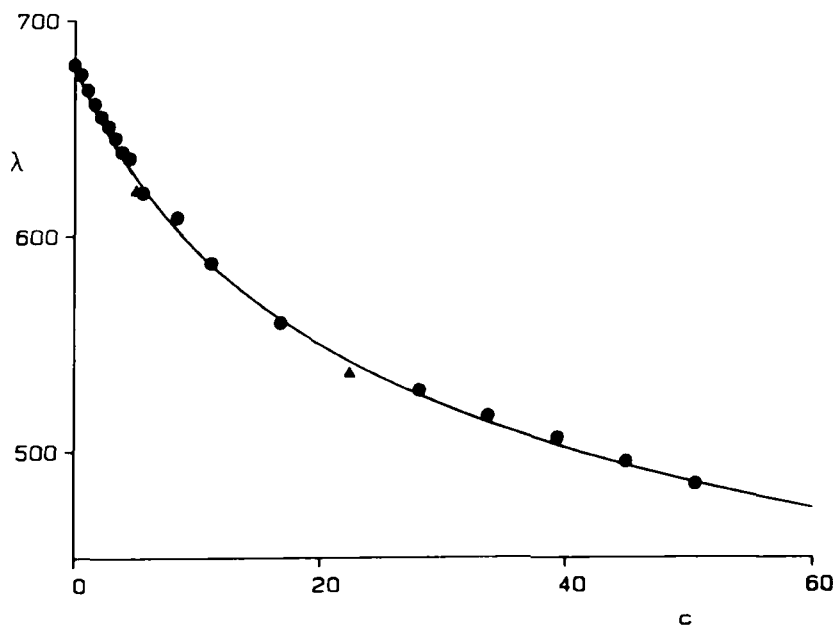
FIG. 1: Relation between the peak shift of dye 1 (λ_{max} in nm) and the content of water (c in mol/l) for DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone).

shift or the $E_T(30)$ values and the water content gives very non-linear calibration plots; see for example the typical relation between the water content c and λ_{max} for DMPU as given in Fig. 1. This handicap has prevented the general use of the method, although calibration curves have been measured for some mixtures of solvents with water.[3-7]

THEORETICAL

The problem with the non-linear plots can be solved by the application of the two-parameter-equation (2),[8-12] which was found to be a general description of the polarity of a binary mixture as a function of its composition.[13,14] In equation (2) c is the molar concentration of the more polar component, $E_T(30)$ the polarity of the binary mixture and $E_T(30)^O$ the polarity of the pure component with lower polarity (anhydrous solvent). E_D and c* are the parameters of the equation. For the determination of water in organic solvents c is the concentration of water. For practical applications, equation (1) and (2) are transformed to equation (3) with $E^{\#}$ = 28590 [kcal·nm]/E_D. This gives a further, and essential, simplification for the procedure of determining water.

$$E_T(30) = E_D \ln (c/c^* + 1) + E_T(30)^O \qquad (2)$$

$$c = c^{\#} \cdot \exp (E^{\#}/\lambda_{max} - E^{\#}/\lambda^{O}_{max}) - c^{\#} \qquad (3)$$

c in equation (3) is the concentration of water in mg/ml or mol/l corresponding to the dimension of $c^{\#}$. $c^{\#}$ is the c* value in the dimension of c. λ_{max} is the absorption wavelength of the pyridiniumphenolate betaine 1 in the water-containing solvent and λ^{O}_{max} is
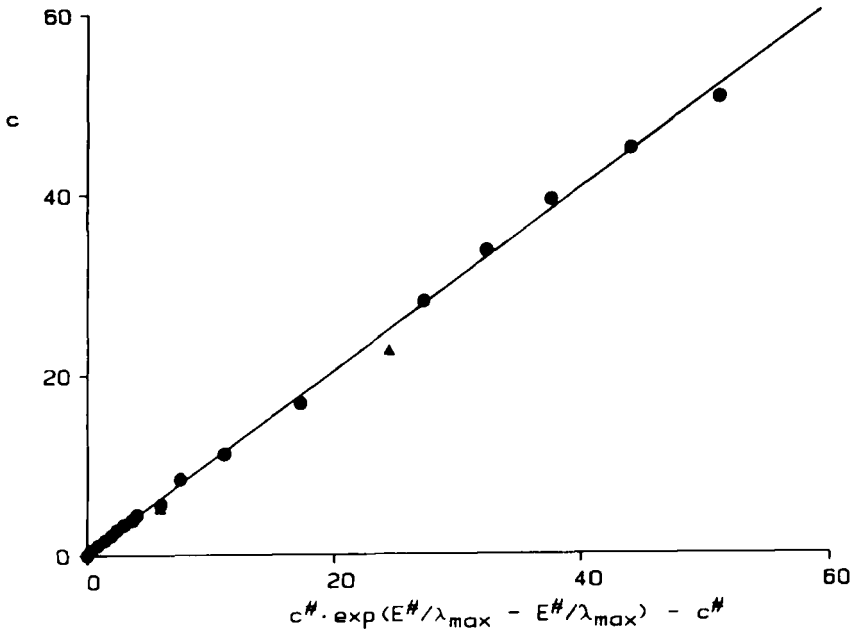
FIG. 2: Linear plot of $c^{\#}$ · exp $(E^{\#}/\lambda_{max} - E^{\#}/\lambda^{0}_{max})$ - $c^{\#}$ versus c of water according to equation (3) for the determination of water in DMPU. c in mol/l and λ_{max} in nm.

the λ_{max} value of the pure dry solvent. $E^{\#}$ is given above. The validity of equation (3) is demonstrated by the linear calibration plot of Fig. 2.

The parameters $E^{\#}$, $c^{\#}$, and λ^{0}_{max} are given in table 1 for a number of frequently used solvents for the pyridiniumphenolate betaine 1.

TABLE 1

Parameters of equation (3) and dye 1 for frequently used solvents[15] at 20°C.

solvent	$c^{\#}$ [mol/l] (mg/ml)	$E^{\#}$ [nm]	λ^{o}_{max} [nm]	$E^{\#}/\lambda^{o}_{max}$ a) c_{min}	r n
acetone	0.664 (12.0)	7960	677.5	11.7 0.21	0.9994 11
acetonitrile	0.293 (5.28)	10600	625.5	16.9 0.15	0.9992 11
1-butanol	1.98 (35.7)	21500	574.1	37.4 2.4	0.9981 22
tert-butyl alcohol	1.01 (18.2)	10100	660.3	15.3 0.43	0.9967 26
N-tert-butyl-formamide	28.2 (508)	5830	567.3	10.3 9.3	0.9965 21
tert-butylhydro-peroxide[16]	0.340 (6.13)	20100	575.3	34.9 0.38	0.9984 10
dimethoxyethane	0.301 (5.42)	9530	748.4	12.7 0.093	0.9996 12
N,N'-dimethyl-acetamide	5.28 (95.1)	5510	664.9	8.29 1.2	0.9984 13
DMEU[b,c]	11.0 (198)	3010	672.7	4.47 1.3	0.9992 20

(Continued)

(Table 1. Continued)

solvent	$c^{\#}$ [mol/l] (mg/ml)	$E^{\#}$ [nm]	λ^{o}_{max} [nm]	$\dfrac{E^{\#}/\lambda^{o}_{max}}{c_{min}}$[a)	r n
1,4-dioxane	0.512 (9.22)	6600	794.2	8.31 0.097	0.9993 27
DMF	11.52 (208)	2990	654.2	4.57 1.5	0.9979 18
DMPU[c,d]	12.8 (230)	2714	679.50	3.99 1.4	0.9996 18
DMSO	53.8 (969)	1190	633.9	1.88 2.9	0.9997 20
ethanol	38.1 (686)	4550	549.8	8.28 10	0.9998 30
formamide	34.3 (618)	5120	511.4	10.0 12	0.9962 10
HMPA[e]	1000 (18020)	50.8	699.0	0.0727 1.9	0.9989 6
methanol	150 (2700)	1600	516.1	3.10 16	0.9300 25
2-methoxyethanol	12.4 (223)	15900	547.7	29.0 12	0.9802 10
N-methylpyrro-lidone[c]	17.4 (313)	2320	677.5	3.42 1.6	0.9996 18
nitromethane	1000 (18020)	6.92	617.5	0.0112 0.33	0.9997 3

(Table 1. Continued)

solvent	$c^{\#}$ [mol/l] (mg/ml)	$E^{\#}$ [nm]	λ^{o}_{max} [nm]	$E^{\#}/\lambda^{o}_{max}$ c_{min} a)	r n
1-propanol	4.22 (76.0)	16900	566.1	29.9 4.1	0.9956 25
propylene carbonate	0.502 (9.04)	9264	621.5	14.9 0.22	0.9990 9
pyridine	5.48 (98.7)	4030	711.2	5.67 0.79	0.9960 29
THF	0.449 (8.09)	7090	764.4	9.28 0.099	0.9997 20
TMU$^{f)}$	4.02 (72.4)	4910	697.3	7.04 0.74	0.9986 14

a) minimal concentration of water in mg/ml detectable with a routine spectrometer with 1 nm resolution. [17] – b) 1,3-dimethyl-2-imidazolidinone. c) substitute of HMPA. – d) 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone – e) caution [18,19] – highly toxic! – f) tetramethylurea.

DETERMINATION OF WATER

The determination of water can easily be carried out – a small amount of the solvatochromic pyridin-iumphenolate betaine is dissolved in the solvent sample so that the extinction of the long wavelength λ_{max} of dye 1 lies between 0.7 and 1.0. λ_{max} is determined

and the content of water is calculated by means of equation (3) and the parameters of table 1. The accuracy of the method depends only on the precision of the spectrometer and the magnitude of $c^{\#}$ and is typically of the order of 5% at a water content of 10 mg/ml with spectrometers having 1 nm resolution. The sensitivity of the determination of water in acetonitrile which is obtained with such a spectrometer is for example 0.2 mg/ml. The $c^{\#}$ value is important for the error of the determination. For $c < c^{\#}$ the absolute error in the concentration determination is constant, whereas for $c > c^{\#}$ the relative error is constant; for a more detailed discussion see ([8-10]) and see below.

For high precision water determinations the maximum wavelength (λ_{max}) must be measured with high accuracy. This could be done by the calculation of the first derivative of the uv/vis spectrum. However, this would result in a decrease of the signal to noise ratio of the spectrometer[20] and would give higher uncertainties in the determination method. Therefore, better results are obtained by applying Mathias' rule,[21] which connects the half-radii of the secants according to Fig. 3. A calibration of the spectrometer should
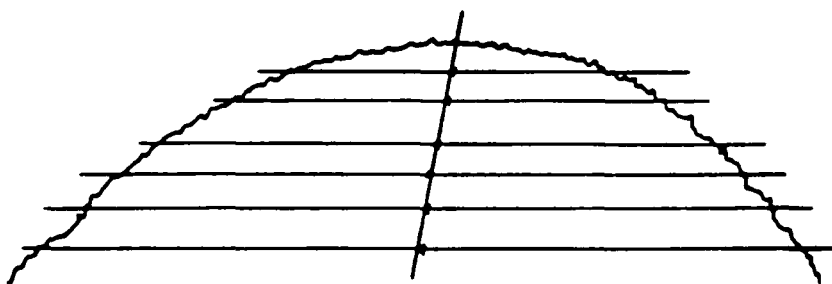
FIG. 3: The precise localisation of λ_{max} of a broad absorption band by the use of Mathias rule - the lines should be drawn in the region of 10 to 15 % from E_{max}.

be done with holmium glass[22] and Mathias' rule

directly before and after the determination.

The parameters of equation (3) for frequently

used solvents and dye **1** are given in table 1. The pa-

rameters for further solvents can be easily measured

in the known manner.[14]

DETECTION LIMITS AND EXPERIMENTAL ERROR

The sensitivity and experimental error of the wa-

ter determination method is essentially given by the

accuracy of the spectrometer. For routine spectrome-

ters with an accuracy of 1 nm the detection limit is

typically as low as 1 mg water in 1 ml solvent; see

table 1. The determination of water is less sensitive

for solvents with high polarity like methanol, and has
a sensitivity better than 0.1 mg water in 1 ml for
solvents of low polarity like 1,4-dioxan or THF.

The error of the water determination can be esti-
mated by Gauß' law of propagation of error.[9,10] The
most important term is the error in the determination
of λ_{max} ($\Delta\lambda_{max}$).[9] This contribution to the complete
error is obtained by equation (4).

$$\Delta c = E^{\#} \cdot \lambda^{-2}_{max} \cdot (c + c^{\#}) \cdot \Delta\lambda_{max} \qquad (4)$$

It is important for the determination of water
that the relative error in c according to equation (4)
is nearly constant for concentrations larger than $c^{\#}$,
whereas the absolute error is nearly constant for
$c < c^{\#}$.

The determination of water by the use of dye 1
can be carried out with nearly all solvents. Even oxy-
dizing solvents like tert-butyl hydroperoxide[17] can be
analysed.

Problems are given by the low solubility of 1 in
aliphatic hydrocarbons. The dye should be replaced by
its penta-tert-butyl derivative[23] which has a higher
solubility in these solvents. However, for this dye,
the parameters of (3) are different from the values
given in table 1.

A further limitation for dye 1 is the analysis of acidic solvents like acetic or formic acid, which protonate the oxygen. Dye 1 should be replaced for these solvents by some other polarity probe, for example 2 (see below). Traces of acids in solvents can be removed by shaking the solvent with calcium carbonate or adding a little base like piperidine.

For very high water contents, with some solvents for more than 100 mg/ml and others more than 400 mg/ml, there is a sudden change in solvent structure giving a second linear correlation with equation (3), but with different parameters $E^{\#}$, $c^{\#}$ and λ_{max}^{o}.[14] This has to be taken into account with solvent analysis with a high content of water.

DETERMINATION OF WATER BY A SIMPLE COLOUR TEST

For a rough routine test for the water content of a solvent, a comparison of the colour of the dye solution with a colour scale of absorption wavelengths is sufficient and can give the wavelength to an accuracy of between 5 and 10 nm when the dye concentration is not very high and the person doing the test is experienced in colour comparison. Colour scales, absorption wavelength and colour, are given, for example, in[24-25].

FURTHER EXTENSIONS

The validity of equation (2) and (3) is well
established for a number of polarity scales;[14] there-
fore the determination of water can be carried out
with these other polarity probes. The advantage of dye
1 is the high sensitivity of the solvatochromism ver-
sus solvent polarity. Therefore dye 1 should be used
for all routine water determinations. Problems come
about when the samples do not have good optical qua-
lity, for example turbid liquids; dye 1 should be re-
placed in these cases by the solvatochromic fluo-
rescent dye 2.[10]

λ_{max} of the fluorescence can easily be determined
even without a fluorescence spectrometer by a simple
three-point-method.[10]

Equation (3) can also be applied for other physi-
cal effects. This has been done for the density and
the index of refraction.[11] With gases a concentration
determination with an accuracy of 10 ppm is possible
by a simple pressure measurement.[12]

EXPERIMENTAL PROCEDURE

For the determination of water a little of dye 1
is dissolved in a cuvette with the solvent under test
(about 1 mg for standard cuvettes) so that the extinc-

tion at λ_{max} lies between 0.75 and 1.0. λ_{max} is precisely localised by means Mathias' rule and the water content calculated with equation (3) by the use of the parameters of table 1.

For example, a sample of THF gives with dye **1** an absorption at 641.8 nm. With $c^{\#}$ = 8.09 mg/ml, $E^{\#}$ = 7090 nm and λ^{O}_{max} = 764.4 nm from table 1 a water content of 39.5 mg/ml is calculated. The given water content is 40 mg/ml and the calculated experimental error 1.3%.

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