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## Density and Viscosity Measurements of Natural Solutions

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# Density and Viscosity Measurements of Natural Solutions†

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Utilizing sophisticated equipment, densimetric and viscosimetric measurements were carried out on samples of ground-waters of Apulia.

Experimental data, utilized to check if simple equations can evaluate the density and the viscosity of multicomponent solutions, confirm the validity of the hypothesis.

#### INTRODUCTION

The assessment of irrigation water quality is an essential and primary step in the development of any irrigation enterprise. However little attention has generally been given to this essential prerequisite in feasibility studies of irrigation (Cass, 1982).

Since most chemical, biochemical and chemico-physical reactions at the interfaces of the soil-water-plant system are strongly affected by ionic activities analytical concentrations must be converted to thermodynamic ones (Ham, 1970; Sposito, 1981; Stumm and Morgan, 1970).

<sup>&</sup>lt;sup>†</sup> Presented at the Symposium on Analytical Problems in the Marine Environment, Genoa, 23-24 May 1983.

This purpose can be achieved by using phenomenological equations, like Debye-Hückel and Davies relationships (Polemio *et al.*, 1980; Sposito, 1980; Stumm and Morgan, 1970) that need the knowledge of ionic strength, a tedious and laborious parameter to obtain.

Therefore several authors (McIntyre, 1980; Sposito, 1981) suggested in the past some correlations between ionic strength (I) and electrical conductivity (EC). Our previous results in this field (Polemio *et al.*, 1978; Polemio *et al.*, 1980) showed a rather high discordance between experimental and calculated I values. In this context the determination of other chemico-physical parameters, like density and viscosity seems very useful (Kestin, 1981; Kestin and Shalkland, 1981; Krumgaltz and Millero, 1982; Yusofova *et al.*, 1980). In fact several authors proposed equations relating viscosity and ionic strength (Kestin and Shalkland, 1981; Yusofova *et al.*, 1980). Analogous relations may exist between density and ionic composition (Chen *et al.*, 1980; Krumgaltz and Millero, 1982). Moreover density and viscosity measurements are rapid and simple by means of new equipments (Eicher and Zwolinski, 1971; Leopold and Jelinek, 1977) like electrical conductivity.

#### MATERIALS AND METHODS

The measurements were carried out on samples of ground waters of Apulia which is a long peninsula composed of fissured limestone.

The most significant physico-chemical properties, i.e., pH, electrical conductivity, ionic strength and composition are reported in Table I. The values of ionic strength, correlated for the ions pairing  $(I_c)$ , was calculated through a FORTRAN program (Bufo *et al.*, 1977).

#### DENSITY MEASUREMENTS

Density measurements were carried out with an Antoon Paar DMA 02C, based on the working principle described by H. Leopold (1977) according to which the density measurement can be made by determining the oscillation period of a mechanical system including

|   |  |                       | D                     | EN                    | <b>1S</b> ]           | IT                    | Y                     | A١                    | ٧D                    | 7                     | /15                   | C                     | S                     | IT                    | Y                     | M                     | E/                    | S                     | UF                    | E                     | MI                    | EN                    | TS                    | 5                     |                       |                       |                       |                       | 18                    | 9                     |
|---|--|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|   | $\sup_{(g  \cdot  l^{-1})}$                        | 0.2210                | 0.2160                | 0.2110                | 0.2110                | 0.2160                | 0.2020                | 0.1870                | 0.2020                | 0.0384                | 0.2020                | 0.2020                | 0.1920                | 0.2020                | 0.2010                | 0.0528                | 0.2010                | 0.0672                | 0.1050                | 0.0096                | 0.0384                | 0.1680                | 0.1680                | 0.1480                | 0.0096                | 0.1680                | 0.2020                | 0.1680                | 0.1920                | 0.1820                |
|   | $HCO_3$<br>(g · l <sup>-1</sup> )                  | 0.2260                | 0.3420                | 0.3660                | 0.3110                | 0.3660                | 0.3720                | 0.3780                | 0.3780                | 0.3170                | 0.3720                | 0.3660                | 0.3720                | 0.3720                | 1.0430                | 0.7690                | 1.0600                | 0.6490                | 0.6840                | 0.8720                | 0.1630                | 0.5300                | 0.3930                | 0.1630                | 0.8890                | 0.1460                | 0.3170                | 0.2870                | 0.3420                | 0.3720                |
|   | $\underset{\left(g\cdot l^{-1}\right)}{\text{cl}}$ | 0.7590                | 0.7370                | 0.8380                | 0.7440                | 0.7760                | 0.7510                | 0.7300                | 0.7550                | 0.0673                | 0.8390                | 0.7660                | 0.7370                | 0.7660                | 0.7650                | 0.0709                | 1.3430                | 0.3450                | 0.6410                | 0.0283                | 0.0354                | 0.7720                | 0.7790                | 0.7720                | 0.0709                | 0.7520                | 0.8130                | 0.7230                | 0.7590                | 0.7520                |
|   | $\underset{(g \cdot l^{-1})}{Mg}$                  | 0.0923                | 0.0875                | 0.0899                | 0.0935                | 0.0972                | 0.1030                | 0.1140                | 0.0948                | 0.0510                | 0.0959                | 0.0923                | 0.0911                | 0.0935                | 0.0935                | 0.0364                | 0.1150                | 0.0522                | 0.0716                | 0.0303                | 0.0145                | 0.0886                | 0.0874                | 0.0874                | 0.0133                | 0.0920                | 0.1000                | 0.0900                | 0.0910                | 0.1000                |
|   | $\underset{(g \cdot l^{-1})}{Ca}$                  | 0.0922                | 0.1380                | 0.1460                | 0.1160                | 0.1360                | 0.1140                | 0.1000                | 0.1360                | 0.0400                | 0.1400                | 0.1420                | 0.1380                | 0.1420                | 0.2420                | 0.0460                | 0.1220                | 0.0460                | 0.0581                | 0.0581                | 0.0801                | 0.0841                | 0.0741                | 0.1222                | 0.0901                | 0.0640                | 0.1230                | 0.1020                | 0.1330                | 0.1280                |
|   | $\overset{K}{(g\cdot l^{-1})}$                     | 0.0235                | 0.0235                | 0.0274                | 0.0235                | 0.0235                | 0.0274                | 0.0235                | 0.0235                | 0.0078                | 0.0274                | 0.0274                | 0.0235                | 0.0274                | 0.0273                | 0.0117                | 0.0469                | 0.0156                | 0.0195                | 0.0039                | 0.0039                | 0.0234                | 0.0234                | 0.0234                | 0.0039                | 0.0120                | 0.0130                | 0.0120                | 0.0120                | 0.0120                |
|   | $\underset{\left(g\cdot l^{-1}\right)}{Na}$        | 0.3840                | 0.3840                | 0.3790                | 0.3790                | 0.3950                | 0.3790                | 0.3610                | 0.3790                | 0.0388                | 0.3790                | 0.3790                | 0.3650                | 0.3750                | 0.3740                | 0.0367                | 0.7300                | 0.1900                | 0.3440                | 0.0160                | 0.0160                | 0.3790                | 0.3790                | 0.3790                | 0.0168                | 0.3750                | 0.4000                | 0.3600                | 0.3750                | 0.3650                |
|   | $\mathbf{Ic}$ (mol $\cdot \mathbf{I}^{-1}$ )       | $2.67 \times 10^{-2}$ | $2.84 \times 10^{-4}$ | $2.71 \times 10^{-2}$ | $3.29 \times 10^{-2}$ | $2.72 \times 10^{-2}$ | $2.82 \times 10^{-2}$ | $2.73 \times 10^{-2}$ | $2.78 \times 10^{-2}$ | $2.81 \times 10^{-2}$ | $1.01 \times 10^{-2}$ | $2.89 \times 10^{-2}$ | $2.78 \times 10^{-2}$ | $2.79 \times 10^{-2}$ | $2.81 \times 10^{-2}$ | $1.21 \times 10^{-2}$ | $4.65 \times 10^{-2}$ | $1.93 \times 10^{-2}$ | $2.77 \times 10^{-2}$ | $1.19 \times 10^{-2}$ | $7.18 \times 10^{-3}$ | $2.91 \times 10^{-2}$ | $2.86 \times 10^{-2}$ | $2.89 \times 10^{-2}$ | $1.28 \times 10^{-2}$ | $2.69 \times 10^{-2}$ | $2.88 \times 10^{-2}$ | $2.70 \times 10^{-2}$ | $2.78 \times 10^{-2}$ | $3.02 \times 10^{-2}$ |
| i | $I \pmod{\cdot l^{-1}}$                            | $3.80 \times 10^{-2}$ | $4.08 \times 10^{-6}$ | $4.04 \times 10^{-2}$ | $6.71 \times 10^{-2}$ | $3.94 \times 10^{-2}$ | $4.21 \times 10^{-2}$ | $3.90 \times 10^{-2}$ | $3.98 \times 10^{-2}$ | $4.11 \times 10^{-2}$ | $1.15 \times 10^{-2}$ | $4.25 \times 10^{-2}$ | $4.13 \times 10^{-2}$ | $4.01 \times 10^{-2}$ | $4.12 \times 10^{-2}$ | $1.46 \times 10^{-2}$ | $6.38 \times 10^{-2}$ | $2.25 \times 10^{-2}$ | $3.33 \times 10^{-2}$ | $1.35 \times 10^{-2}$ | $8.20 \times 10^{-3}$ | $3.88 \times 10^{-2}$ | $3.71 \times 10^{-2}$ | $3.71 \times 10^{-2}$ | $1.45 \times 10^{-2}$ | $3.44 \times 10^{-2}$ | $4.15 \times 10^{-2}$ | $3.65 \times 10^{-2}$ | $3.99 \times 10^{-2}$ | $3.90 \times 10^{-2}$ |
|   | C.E.<br>$(\mu S \cdot cm^{-1})$                    | 2660                  | 2750                  | 2870                  | 2700                  | 2880                  | 2750                  | 2680                  | 2760                  | <b>66</b> 0           | 2800                  | 2800                  | 2650                  | 2800                  | 2800                  | 620                   | 4300                  | 1420                  | 2190                  | 530                   | 580                   | 2640                  | 2600                  | 2770                  | 580                   | 2500                  | 2550                  | 2650                  | 2550                  | 2700                  |
|   | Hq   | 7.85                  | 7.6                   | 7.1                   | 7.55                  | 7.15                  | 7.4                   | 7.6                   | 7.2                   | 6.8                   | 7.9                   | 7.9                   | 7.2                   | 7.2                   | 7.2                   | 7.9                   | 7.4                   | 7.8                   | 7.7                   | 7.3                   | 6.9                   | 7.9                   | 7.8                   | 7.4                   | 7.0                   | 7.8                   | 8.0                   | 7.8                   | 7.6                   | 7.4                   |

TABLE I Physico-chemical properties of the examined waters

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the well defined volume of the liquid contained in the measurement cell being examined.

The volume of the cell has to be strictly constant for the solution to be examined and for the reference standard (pure water, air). The oscillating part, that fills with a syringe, is a glass tube (Figure 1) put in a metallic block which is thermostated in an extremely accurate way. The instrument is calibrated by determining its constant at 25°C through the oscillation period of both the distilled water and air whose densities are well known. Afterwards, the solution density is calculated by determining the oscillation period of any liquid. The system is thermostated with an accuracy of  $\pm 0.005$ °C. After calibration of the equipment the densities of some standard solvents of very high purity (benzene, CCl<sub>4</sub> etc.) were, from time to time, determined and compared with the literature values.

#### **VISCOSITY MEASUREMENTS**

The measurements have been made by a suspended level viscosimeter (type Ubbelhode) coupled with an automatic viscosity system (AVS/G and AVS/S) manufactured by Scott (Figure 2). The system, through two photocells externally applied to the viscometer, allows determination of the efflux time of the solution, without the operator. The instrument is previously calibrated through the time measurements of the distilled water whose viscosity value is well known. Afterwards, the viscosity is determined by the formula:

$$\eta = A\rho t - \frac{B\rho}{t} \tag{1}$$

where  $\eta$  is the solution viscosity expressed in centipoise,  $\rho$  is its density expressed in g cm<sup>-3</sup> (previously measured), t is the efflux time in seconds and A and B are two characteristic constants of the viscometer used, previously calculated. All the parameters i.e. the perfect perpendicularity of the measurement cell, the thermostatic time of the solution (not less that 20 minutes), the repetition of the efflux times for at least 7 times with a maximum deviation of 0.04 sec, make it possible to obtain viscosity values with a precision greater than 0.01%. As regard the density measurements, the essential condition for viscosity measurements with the desired precision is to obtain a thermostatation of the bath, where the viscometer is immersed, of  $\pm 0.005^{\circ}$ C with respect to the temperature value under examination (25°C in our case). Such precise temperature values were obtained which regulating system of 'Lauda' and were checked with a platinum probe thermometer.



FIGURE 2 Viscometer system.

### **EXPERIMENTAL RESULTS**

Table II gives experimental density and viscosity values. The data were utilized to check if simple relationships such as:

$$d = d_{0} + a |Na^{+}| + b |K^{+}| + c |Ca^{++}| + d |Mg^{++}|$$
  
+  $e |Cl^{-}| + f |HCO_{3}^{-}| + g |SO_{4}^{-}|$  (2)  
$$\eta = \eta_{0} + a' |Na^{+}| + b' |K^{+}| + c' |Ca^{++}| + d' |Mg^{++}|$$
  
+  $e' |Cl^{-}| + f' |HCO_{3}^{-}| + g' |SO_{4}^{-}|'$  (3)

(where  $d_0 = 0.99704$  (Kell, 1967) and  $\eta_0 = 0.8902$  (Eicher and

|              |        |    | TABLE   | II I |           |    |          |
|--------------|--------|----|---------|------|-----------|----|----------|
| Experimental | values | of | density | and  | viscosity | of | examined |
|              |        |    | water   | S    |           |    |          |

| Density $(g cm^{-3})$ | Viscosity (poise) |
|-----------------------|-------------------|
| 0.99856               | 0.8959            |
| 0.99853               | 0.8952            |
| 0.99858               | 0.8968            |
| 0.99847               | 0.8958            |
| 0.99860               | 0.8956            |
| 0.99844               | 0.8960            |
| 0.99844               | 0.8954            |
| 0.99857               | 0.8954            |
| 0.99747               | 0.8961            |
| 0.99853               | 0.8921            |
| 0.99858               | 0.8953            |
| 0.99854               | 0.8955            |
| 0.99863               | 0.8952            |
| 0.99863               | 0.8955            |
| 0.99743               | 0.8917            |
| 0.99927               | 0.8968            |
| 0.99779               | 0.8937            |
| 0.99818               | 0.8969            |
| 0.99740               | 0.8928            |
| 0.99741               | 0.8932            |
| 0.99841               | 0.8953            |
| 0.99837               | 0.8954            |
| 0.99851               | 0.8959            |
| 0.99744               | 0.8930            |
| 0.99838               | 0.8958            |
| 0.99862               | 0.8980            |
| 0.99848               | 0.8988            |
| 0.99856               | 0.8987            |
| 0.99859               | 0.8969            |

|                               | Density                              | Viscosity                          |  |  |  |  |  |  |  |
|-------------------------------|--------------------------------------|------------------------------------|--|--|--|--|--|--|--|
| Relative standard deviation r | 0.2586 × 10 <sup>-5</sup><br>0.99677 | $7.3321 \times 10^{-4}$<br>0.98182 |  |  |  |  |  |  |  |

 TABLE III

 Values of the relative standard deviations and of the correlation coefficients of the density and viscosity

Zwolinski, 1971) are the density and the viscosity of  $H_2O$  at 25°C respectively) can evaluate the density and the viscosity of multicomponent solution.

The equations were calculated through successive iterations.

In Table III the values of the relative standard deviations and the correlation coefficients are reported (r).

#### CONCLUSIONS

These preliminary results confirm the validity of the model and show a need to broaden the study in order to provide the immediate and reliable informations about the properties of natural solutions.

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