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Effect of concentration and temperature on the interactions between saline soil salts and nitro phosphate fertilizer under atmospheric pressure: A thermo-acoustic approach

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ABSTRACT

A decrease in the ability of the plants to absorb nutrients usually takes place in saline soils. Application of fertilizers corrects nutrients deficiencies and decreases the adverse effects of saline salts on the plants. The present work is aimed to study the interactions of fertilizer with saline salts in aqueous solutions to explore the role of fertilizer on soil fertility by controlling soil salinity in terms of fertilizer-salt interactions. Density and speed of sound of nitrophosphate in water and in saline salts solutions of different concentrations has been measured at different temperatures. Thermo acoustical parameters like apparent and partial molar volume, partial molar expansibility and Hepler's constant, compressibility factor and intermolecular free length have been calculated. Positive values of apparent molar volume (V_Φ) and negative values of apparent and partial molar compressibility (K_Φ and K_Φ^o)of fertilizer in solutions showed strong intermolecular interactions in solutions. Positive values of Hepler's constant indicate the structure making behavior of fertilizer in water and in saline salt solutions.

1. Introduction

Soil is a medium for plant growth which is affected by soil type and its physiological characters. The soil's physical properties affect its capability to supply nutrients and water to the plant [1]. The soil with high content of salts is called saline soil. Salts (cations or anions) in soil are found in either as dissolved form in soil solutions, as adsorbed salts in the form of adsorbed complexes or as precipitated salts. Mostly, in saline soil high concentration of Na^+, Ca^{+2}, Cl^- and K^+ ions is present and these saline salts may also affect the crop yield and plant growth [2]. Moreover, the salinity also causes problems in biochemical properties of the land [3].

Irrigation of soil is considered as a best solution to reduce soil salinity. Moreover, agronomical studies deal with response of a particular crop to the addition of fertilizer in saline soil. Hence fertilizers are also used to reduce salinity problems in soil, which counteract the adverse effect of soil salinity, sodicity, or water logging on the production of a particular crop in a specified soil. Numerous factors are involved in plant response to fertilizers under saline, sodic, or waterlogged conditions so a suitable fertilizer should be used for this purpose. Efficiencies of fertilizers applied to salt affected soils are lower than when applied to non-saline soils. In salt affected soil, ability of the plants to absorb nutrients like potassium, phosphorus or ammonium ions reduces [4–7].

Application of fertilizers containing K, NH_4 or P fertilizers not only cover their deficiencies but also decreases the adverse effects of Na, Cl, or SO_4^{-2} on the plants [8,9].

Through literature survey, it has been revealed that various studies have been done to investigate the role of phosphate fertilizers to enhance the crop production, and their role in heavy metal uptake and detoxification of toxic metals has been studied. Further experiments have been performed for the identification and quantification of specific forms of organic P in organic fertilizers and soils [6–8]. Recently, role of a phosphate fertilizer (Triple super phosphate) in order to remove or to reduce soil salinity have also been investigated in terms of intermolecular interactions prevailing among fertilizers molecule and soil salts (e.g. Cl^-, Na^+, HCO^{3-}, SO_4^{2-} etc.) [9].

In the present study interactions between fertilizer ions and saline salts have been explored in the presence of saline solutions of NaCl, $NaHCO_3$ and Na_2SO_4. Fertilizer used for this purpose is nitrophosphate which contains high proportion of nitrogen and phosphorus. Chemical formula of nitrophosphate is H_2NO_6P. Present study deals with thermo acoustical properties of fertilizer obtained from density and sound velocity data of fertilizer solutions in water and saline salts solutions. These parameters are indicative of solute-solute and solute-solvent interactions and can vary by varying temperature but do not alter or disturb the chemical structure of molecules in the system [10].

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2. Experimental

2.1. Materials

Nitrophosphate, sodium chloride, sodium sulfate, and sodium bicarbonate, product of Sigma, were used as received without any purification. All glassware was carefully washed with de-ionized water, cleaned and dried in oven before use. Double distilled de-ionized water with conductivity of $1.5 \times 10^{-4}\ \Omega^{-1}\ m^{-1}$ was used for the preparation of solutions. Specifications of chemicals used in experiment have been given in Table 1.

2.2. Methods

Density and sound velocity of fertilizer solutions ($0.0042\ mol \cdot kg^{-1}$–$0.0384\ mol \cdot kg^{-1}$) in water and in saline salts (NaCl, Na_2SO_4 and $NaHCO_3$) of varying concentrations (for Na_2SO_4 0.0141, 0.0281, 0.0422, 0.0563 and 0.0704 $mol \cdot kg^{-1}$, for $NaHCO_3$ 0.0238, 0.0476, 0.0714, 0.0952 and 0.1190 $mol \cdot kg^{-1}$, for NaCl 0.0342, 0.068, 0.1026, 0.1367 and 0.1709 $mol \cdot kg^{-1}$) were measured at different temperatures (293.15K–313.15K) and at 101 kPa pressure by an Anton Paar density and sound velocity analyzer DSA 5000 M. The sample density is determined by measuring the oscillation frequency of a U-shaped sample tube completely filled with the sample liquid. The principle of sound velocity measurement is based on propagation time technique. The sample is sandwiched between two piezoelectric ultrasound transducers. One transducer emits sound waves through the sample-filled cavity (frequency around 3 MHz) and the second transducer receives those waves [11]. Thus, the sound velocity is obtained by dividing the known distance between transmitter and receiver by the measured propagation time of the sound waves up to 0.5 ms^{-1}accuracy and 0.1 ms^{-1}repeatability. The accuracy and repeatability of DSA 5000 M for density are $5 \times 10^{-6}\ gcm^{-3}$ and $1 \times 10^{-6}\ gcm^{-3}$ and that of temperature is 0.01 °C and 0.001 °C respectively. The weighing of chemicals was done by Wiggen Hauser electronic balance with a precision of ± 0.001 mg and reproducibility of ± 0.005 mg. The standard uncertainties in molality (m), density (d), sound velocity (u_s), and temperature (T) and pressure (P) are $\pm 0.0015\ mol \cdot kg^{-1}$, $\pm 1 \times 10^{-6}\ g \cdot cm^{-3}$, $\pm 0.02\ m \cdot s^{-1}$, $\pm 10^{-2}$ K and ± 5 kPa respectively. The measured density and sound velocity data was utilized in determining physic-chemical properties of fertilizer solutions.

3. Results and discussion

3.1. Density and sound velocity measurements

Density and sound velocity of pure water has been measured at temperatures 293.15K–313.15K and measured data has been given in Table 2 with literature reported data at respective temperatures. Comparison of experimental results with literature values showed that our results are in accordance with those reported in literature [11–14].

Density and sound velocity of nitro phosphate solutions at different concentrations in water and in saline salts solutions have been measured at different temperatures (293.15K–313.15K) and obtained data has been given in Tables 3 and 4. From Table 3 it is obvious that density of fertilizer solutions in water and in saline salts (NaCl, Na_2SO_4 and $NaHCO_3$) is increasing with increasing fertilizer concentration which shows enhanced intermolecular interactions in solutions, while density decreases with rise in temperature as with increasing temperature kinetic energy of molecules in solutions dominates over binding energy of solution components and hence solution becomes less dense [15,16]. Sound velocity of aqueous fertilizer solutions increases with increasing fertilizer concentration due to increased cohesion between water and fertilizer molecules. Where with increasing temperature number of collisions in a solution increases leading to increase in ultrasonic velocity [17].

Among three presently used saline salts (NaCl, Na_2SO_4 and $NaHCO_3$), HCO_3^- ions (dissociated from $NaHCO_3$) have least affinity with water molecules due to its smaller charge to size ratio as compared to those of Cl^- and So_4^{-2} ions which take much solvent (water) molecules to hydrate themselves making less availability of solvent molecules for fertilizer molecules to interact with. So, in case of $NaHCO_3$ solution when fertilizer is added to solutions, HCO_3^- ions readily interacts with fertilizer molecules in the solution to develop intermolecular forces because it has least affinity for water molecules in solutions and a large volume of solvent is available for fertilizer molecule to interact with [18].

Table 2
Density $(d_o)/g \cdot cm^3$ and sound velocity $(u_o)/ms^{-1}$ of water at different temperatures and at 101 kPa pressure.

	This work		Literature value	
T/K	$d_o/g \cdot cm^3$	u_o/ms^{-1}	$d_o/g \cdot cm^3$	u_o/ms^{-1}
293.15	0.998202	1482.63	0.998202[a]	1482.94[a]
298.15	0.997025	1497.06	0.997031[b]	1497.00[d]
303.15	0.997748	1509.57	0.995642[a]	1509.10[c]
308.15	0.994258	1519.15	0.994023[c]	1519.57[b]
313.15	0.992567	1529.63	0.992213[b]	1529.30[c]

The standard uncertainties in density (d), sound velocity (u) and temperature (T) and pressure (P) are $\pm 1 \times 10^{-6}$ $g.cm^{-3}$, $\pm 0.02\ ms^{-1}$, $\pm 10^{-2}$ K and ± 5 kPa respectively.
[a] Reference [11].
[b] Reference [12].
[c] Reference [13].
[d] Reference [14].

3.2. Volumetric parameters

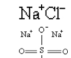
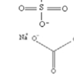
3.2.1. Apparent molar volume

Apparent molar volume (V_ϕ) is the difference between volume of the solution and pure solvent per one mole of solute. Corresponding values of V_ϕ can be calculated from density data using following eq. [19]:

$$V_\phi = M/d + 1000\ (d_o - d)/mdd_o \tag{1}$$

where M is molar mass of fertilizer (142 $gmol^{-1}$), m is the molality of fertilizer solutions in water and in saline salts, d and d_o are densities of solution and solvent respectively. Density of fertilizer (nitrophosphate) solutions in water and saline salts ($NaHCO_3$, NaCl and Na_2SO_4) solutions at different temperatures (293.15K–313.15K) has been used to calculate

Table 1
Specifications of chemicals used in experiment.

Chemical names	Source	Mass fraction purity	Purification method	Chemical structures
Sodium chloride	Sigma Aldrich	>0.995	Used as received	Na^+Cl^-
Sodium sulfate	Sigma Aldrich	0.999	Used as received	
Sodium bicarbonate	Sigma Aldrich	>0.995	Used as received	
Nitro phosphate	Sigma Aldrich	>0.995	Used as received