Journal of Molecular Liquids 225 (2017) 64–86

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

A thermo-acoustical study to explore interactions between soil salts and fertilizer in view to control the soil salinity

Bushra Naseem *, Iqra Arif

Department of Chemistry, Lahore College for Women University, Jail Road, Lahore 54000, Pakistan

A R T I C L E I N F O

Article history:
Received 10 September 2016
Received in revised form 25 October 2016
Accepted 27 October 2016
Available online 16 November 2016

Keywords:
Triple superphosphate
Saline salts
Apparent molar volume
Apparent molar compressibility
Acoustical parameters
Fertilizer-salt interactions

A B S T R A C T

Presence of excess salts in soil poses major problems to agricultural sector. Use of fertilizers is considered as a best solution to reduce soil salinity. The present work is aimed to study the effect of fertilizers on soil fertility in terms of fertilizer-salt interactions. For this purpose triple super phosphate (TSP) is being used which is a major source of phosphate. Density and sound velocity of triple super phosphate molecule and different saline salts were measured at different temperatures using different concentrations of each salt. From the measured experimental data thermo acoustical properties like molar volume, apparent molar isentropic compressibility, etc. were calculated. The effect of different parameters like salt concentration, temperature and fertilizer concentration on thermo acoustical properties of fertilizer solutions was studied and the results were explored in terms of solute-solvent and solvent-solvent interactions. Positive values of apparent molar volume showed strong intermolecular interactions in fertilizer-salt solutions.

1. Introduction

All soils contain some amount of soluble salts. Many of these salts act as a source of essential nutrients for the healthy growth of plants. However, when the quantity of the salts in the soil exceeds a particular value, the growth, yield and quality of most crops are adversely affected to a degree depending upon the kind and amount of salts present, the stage of growth, type of plant, and environmental factors. Thus, soil containing excess amount of salts is called salt affected soil or saline soil [1, 2]. The term salinity refers to the presence of the major dissolved inorganic solutes (essentially Na^+, Mg^{++}, Ca^{++}, K^+, Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}) in the soil. Salinity is quantified in terms of total concentration of such soluble salts [3].

In the field, saline soils can be identified by the presence of white crust of salts on the surface in a dry state. This efflorescence may be wet, fluffy, or solid in consistency and light or dark in color depending upon its main constituents. Abundance of $CaSO_4$ and $CaCO_3$ gives a fine, fluffy, dusty surface, while a mixture of NaCl and Na_2SO_4 gives a crystalline white mass. $MgCl_2$ gives a dark crust that is highly hygroscopic [4–6].

The salinity and sodicity of soil has great effects on nutrients availability to plants and on the ability of plant roots to absorb nutrients. Because of the low productivity problem in the salt affected soils, fertilizers are applied to counteract the conditions which limit the plant absorption of nutrients [7]. Two main approaches are usually encountered to study the fertility – salinity interactions and these are:

1. Physiological Approach
2. Agronomical Approach
   The physiological studies are conducted to find out basic facts which might explain the adverse effects on the plant biological processes and on the absorption of nutrient elements in the presence of known kinds and concentration of salts. While the agronomical studies concern with the response of a crop under specified soil salinity conditions to increments of fertilizers. They are mainly concerned with counteracting the adverse effect of soil salinity, sodicity, or water logging on the production of a particular crop on a specified soil [8,9].
   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.
   A decrease in the ability of the plants to absorb K or NH_4 usually takes place in saline soils containing excess Na, Mg, or Ca. Also, P absorption may be decreased in presence of excess Cl^- or SO_4^-. Application of K, NH_4 or P fertilizers not only corrects their deficiencies but also decreases the adverse effects of Na, Cl, or SO_4^- on the plants [10,11].
   Triple superphosphate (TSP) also known as calcium dihydrogen phosphate containing higher proportion of phosphate ions has chosen for present study to investigate the molecular interactions between fertilizer and salts in saline soil like Cl^- or SO_4^-. Chemical structure of TSP is shown in Fig. 1. K.E. Annaheim et al. studied the

* Corresponding author.
E-mail address: bnbsk@yahoo.co.uk (B. Naseem).

http://dx.doi.org/10.1016/j.molliq.2016.10.143
0167-7322/

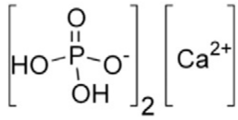

Fig. 1. Structure of triple superphosphate.

effect of long term addition of organic fertilizers on soil organic phosphorus characterized by ^{31}P NMR spectroscopy.

During literature survey it has been revealed that various studies on fertilizer efficiency and their role to enhance the crop production and to lower or remove the soil problems in cultivated areas has been found. Annaheim et al. studied the effect of long term addition of organic fertilizers on soil organic phosphorus characterized by ^{31}P NMR spectroscopy [12]. Similarly, evaluation and role of phosphate fertilizers for the stabilization of cadmium in highly contaminated soils, in heavy metal uptake and detoxification of toxic metals has been studied [13,14], The knowledge of physico-chemical properties of ternary system (water + electrolyte + solute) has great importance in biochemistry and biophysics [15]. Sugars, polyols, and amino acids [16] have received considerable attention in this field, but there is no thermo physical study to investigate the interactions of fertilizer and soil salts. Therefore, the present work is aimed to explore the molecular interactions between phosphate fertilizer (Triple super phosphate) and salts present in saline soil using electrolytic (NaCl, Na_2SO_4, $NaHCO_3$) solutions by volumetric and acoustical approach which can help to understand a strategy for saline soil remediation.

2. Experimental

2.1. Materials

Chemicals, Triple superphosphate (CAS no: 7778-77-0) mass fraction purity > 0.950, sodium chloride (CAS no: 7647-14-5) mass fraction purity > 0.995, sodium sulfate (CAS no: 7757-82-6) mass fraction purity > 0.999 and sodium bicarbonate (CAS no: 144-55-8) mass fraction purity > 0.995 were product of Sigma and 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.

2.2. Methods

Density (d) and sound velocity (u) were measured by an Anton Paar DSA 5000 model high precision vibrating tube digital density meter and ultrasound speed measuring device. The instrument has a built-in thermostat to maintain the temperature with a fundamental frequency of 3 MHz. The accuracy and repeatability of DSA 5000 M for density are 5×10^{-6} gcm^{-3} and 1×10^{-6} gcm^{-3} and that of temperature is 0.01 °C and 0.001 °C respectively. In the same way sound velocity is also measured by the instrument up to 0.5 m/s accuracy and 0.1 m/s repeatability.

Density and sound velocity of pure water and fertilizer solutions of various concentrations (0.0042, 0.0128, 0.0213, 0.0299 and 0.0384 mol kg^{-1}) in saline salt were measured at temperatures (293.15 K–313.15 K) and 101 kPa pressure. The weighing of chemicals was done by Wiggen Hauser electronic balance with a precision of ±0.001 mg. At least three readings of each composition were reproducible to ±0.005 mg and the obtained values were averaged. The measured densities and ultrasound speeds were utilized in determining volumetric and acoustical properties of solutions as described in the next section.

Table 1
Density (d_o)/g cm^3 and sound velocity (u_o)/ms^{-1} of water at different temperatures (T).

T/K	This work		Literature value	
	d_o/g cm^3	u_o/ms^{-1}	d_o/g 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 u are u(d) = $\pm 1 \times 10^{-6}$ g cm^{-3}, u(T) = ±0.01 K, u(s) ± 0.01 m s^{-1}, and u(P) ± 5 kPa.
[a] Reference [17].
[b] Reference [18].
[c] Reference [19].
[d] Reference [20].

3. Results and discussion

3.1. Density and ultrasonic velocity measurement

Density is a measure of compactness of matter within substance and is closely related to packing of materials in the system, so different materials have different densities. Temperature and pressure can change density of material. By increasing pressure density increases while increase in temperature causes a decrease in density [16]. In sound wave, the material undergoes small, localized compressions and expansions. These compressions and expansions resultantly change the density and viscosity of liquids.

In the present work density and sound velocity of pure water has been measured at different temperatures (293.15 K–313.15 K) and the measured data has been given in Table 1. Comparison of measured data with literature reported density and sound velocity data for

Table 2
Molality (m), density (d), apparent molar volume (V_ϕ), partial molar volume (V^o_ϕ) and slope (S_v) of fertilizer (TSP) solutions in water at different temperatures (T).

m/mol kg^{-1}	d/g cm^{-3}	V_ϕ/cm^3 mol^{-1}	$V^o{}_\phi$/cm^3 mol^{-1}	S_v/kg cm ^{3} mol^{-1}
293.15 K				
0.0042	0.998667	123.30		
0.0128	0.999467	135.12		
0.0213	1.000267	136.89	126.16	380.99
0.0299	1.001067	137.91		
0.0384	1.001867	138.18		
298.15 K				
0.0042	0.997471	127.86		
0.0128	0.998251	138.22		
0.0213	0.999031	139.73	130.39	331.43
0.0299	0.999811	140.62		
0.0384	1.000591	140.83		
303.15 K				
0.0042	0.998173	132.87		
0.0128	0.998933	141.41		
0.0213	0.999693	142.57	134.98	269.55
0.0299	1.000453	143.31		
0.0384	1.001213	143.44		
308.15 K				
0.0042	0.994656	139.49		
0.0128	0.995406	144.51		
0.0213	0.996156	144.98	140.78	148.98
0.0299	0.996906	145.43		
0.0384	0.997656	145.39		
313.15 K				
0.0042	0.992947	143.911		
0.0128	0.993677	147.62		
0.0213	0.994407	147.85	144.90	104.17
0.0299	0.995137	148.17		
0.0384	0.995867	148.08		

The standard uncertainties u are u(d) = $\pm 1 \times 10^{-6}$ g cm^{-3}, u(m) = ±0.0015 mol kg^{-1}, u(T) = ±0.01 K, and u(P) ± 5 kPa.