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Solubility and freezing points of Disodium Terephthalate in Water- Ethylene Glycol mixtures

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Abstract

The solubility of disodium terephthalate in aqueous sodium hydroxide and in aqueous sodium hydroxide - ethylene glycol mixtures was determined experimentally by temperature analysis, gravimetry and titration. The experimental results were compared with existing literature data and the phase diagrams were determined from -25 °C to 70 °C. The solubility of disodium terephthalate has no considerable dependence on temperature. The freezing points of disodium terephthalate solutions vary with composition as any other solution. The solubility and freezing points decrease with increasing concentrations of ethylene glycol. Disodium terephthalate is salted out by the addition of sodium hydroxide.

Keywords

Disodium Terephthalate; Ethylene Glycol; Freezing Point Depression; Gravimetric determination; Titrimetric determination; Solid Liquid Equilibrium

1. Introduction

An efficient, sustainable, environment-friendly, and less energy demanding way to industrially recycle polyethylene terephthalate (PET) is in high demand.¹ Due to massive production and widespread application of PET, an enormous amount of PET waste is being generated. As PET is highly resistant to atmospheric and biological degrading agents, it remains a substantial volume fraction in the waste streams. Therefore, PET waste is considered a noxious material.² PET waste therefore poses serious economic and environmental problems.

Recycling plastics and PET materials to produce new products can lead to saving up to 50-60% of capital in comparison with making the same product from the virgin resin³, besides the environmental benefits of this practice. The most sustainable way to recycle PET plastics is the chemical method⁴, and Bartolome *et al.*¹ reviewed principles of chemical recycling. There

are three main mechanisms for chemical recycling of PET: hydrolysis, methanolysis, and glycolysis. Hydrolysis is a method in which PET is depolymerized to terephthalic acid (H_2TP) and ethylene glycol (MEG) in aqueous acidic, alkaline or neutral environment. In addition to virgin grade PET, other expensive chemicals like oxalic acid can also be produced from hydrolysis.⁵ Caustic soda can be used for breaking down PET to terephthalic acid in alkaline environment and this process is called “alkaline hydrolysis”.⁶

The main components in alkaline hydrolysis are ethylene glycol (MEG), terephthalic acid (H_2TP), disodium terephthalate (Na_2TP), sodium hydroxide ($NaOH$) and water (H_2O).⁷ Terephthalic acid (H_2TP) has been extensively studied because it has a broad spectrum of industrial application as valuable raw material for producing different types of polyesters.⁸ Sun *et al.*⁹ examined the stability of H_2TP under high pressure. Takebayashi *et al.*¹⁰ measured the solubility of H_2TP in water up to high temperatures. They showed that the mole fraction solubility of H_2TP in water increases exponentially with increasing temperature from $1.25 \cdot 10^{-5}$ at 349 °K to $12 \cdot 10^{-3}$ at 547 °K at 10 MPa. The solubility of H_2TP in binary solvent mixtures of water and acetic acid was determined by Wang *et al.*¹¹ Besides, Sandhwar and Prasad¹² investigated removal of terephthalic acid from waste-water.

The solubility of Na_2TP is a critical factor in designing the downstream part of a chemical PET recycling plant including solid-liquid separation and purification of the products. Ellingboe and Runnels¹³ determined the solubility of Na_2TP in aqueous solutions of sodium carbonate and sodium bicarbonate applying a combination of titration and gravimetry method. Wallace and Carr¹⁴ reported that sodium hydroxide reduced the solubility of disodium terephthalate in aqueous solutions. In general, the amount of published solid-liquid equilibrium (SLE) data on Na_2TP is quite scarce. Thus, there is a lack of thermodynamic data required to create a modeling basis for PET recovery simulations.

In this work, we experimentally determined the solubility of H_2TP and Na_2TP in water - ethylene glycol mixtures having various $NaOH$ content. The solubility of Na_2TP was determined in different solutions from -25 °C up to 70 °C. Although the recovery processes in a PET recycling plant may be operated at higher temperatures, the data obtained in the present study will be able to support a consistent thermodynamic model for simulation of the processes.

2. Experiments

2.1. Materials

Na_2TP (CAS No.10028-70-3) was purchased from Alfa Aesar, Thermo-Fisher (Kandel), having impurity of $NaOH$. An analysis of its composition is presented in Table 1. We will refer to this product using the abbreviation *AAS*.

Table 1, *AAS* composition

Component	Weight percent 100w / g. (g total) ⁻¹	Mole percent 100m / mole. (mole total) ⁻¹
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Na_2TP	94.14	75.35
$NaOH$	5.86	24.65

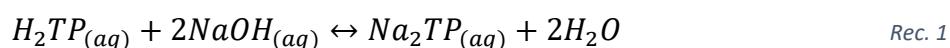
All the other chemicals utilized in this study are listed in Table 2. The solutions were prepared by mixing pure chemicals with deionized water using an analytical scale with an accuracy of ± 0.1 mg.

Table 2, specifications of chemicals

Chemical name	Molecular formula	CAS No.	supplier	Purity (mass percent)	comment
Disodium terephthalate	Na_2TP	10028-70-3	Alfa Aesar, Thermo-Fisher (Kandel)	94.14%	Abbreviated as AAS, referred to Table 1
Terephthalic acid	H_2TP	100-21-0	Sigma Aldrich	98%	
Sodium hydroxide	$NaOH$	1310-73-2	Sigma Aldrich	97%	In pellet form
Ethylene glycol	MEG	107-21-1	VWR chemicals	99.8%	

2.1.1 Synthesis of Na_2TP

Disodium terephthalate was synthesized by first mixing $NaOH$ and H_2TP . Pellets of $NaOH$ and powder of terephthalic acid were added to a container in stoichiometric proportions with slight excess of H_2TP . After that, the mixture was dissolved in deionized water; and the solution was examined not to be super-saturated. It was done by adding a minute amount of H_2TP and checking whether it can be dissolved or not. This reaction (*Rec. 1*) occurred under aqueous conditions as both reactants were dissolved.



The synthesized disodium terephthalate was in the form of an aqueous binary solution containing 2 weight percent $Na_2TP_{(aq)}$.

2.2. Apparatus

2.2.1. Temperature analysis (Freezing Point Depression measurements)

Temperature analysis or Freezing Point Depression experiments were carried out using a modified Beckmann apparatus¹⁵ developed by Fosbøl *et al.*¹⁶. Solids were dissolved in different solvents by shaking in Thermo Scientific MaxQ 4450 incubator shaker for at least 24 hours.

2.2.2. Gravimetric determination of Na_2TP solubility

The gravimetric determinations were conducted by an experimental setup, which was introduced and examined by Murcia *et al.*¹⁷. For filtration, we used grade GF/D glass

microfiber filters with a particle retention size of 2.7 μm . The filters were produced by Whatman from General Electric. A Heraeus incubator was utilized to dry the samples.

2.2.3. Titrimetric determination of Na_2TP solubility

A procedure similar to the one used by Fosbøl *et al.*¹⁸ was applied to determine the solubility of Na_2TP . For this set of experiments, syringe filters provided by Whatman International Ltd. with a pore size of 0.2 μm were used. The filter media was PTFE housing with polypropylene. 0.5 molar HCl provided by Alfa Aesar was used as the titrant. Automatic titrations were carried out with a Titrando 888, produced by Metrohm (Switzerland).

2.3. Experimental methods

2.3.1. Temperature analysis experiments

Two sets of assays were made, one with *AAS* and the other with synthesized Na_2TP . In one set, *AAS* was added to various mixtures of MEG and *NaOH* in water. Several quaternary aqueous solutions of disodium terephthalate, ethylene glycol and sodium hydroxide ($\text{Na}_2\text{TP} + \text{NaOH} + \text{MEG} + \text{H}_2\text{O}$) were prepared. The mixtures were kept in the Thermo Scientific incubator shaker fixed at 25 °C for at least 24 hours. Then, the samples in which the solutes dissolved completely were collected; samples with undissolved material were discarded. The possibility of super-saturation was examined by adding a very small amount (about 0.1 g) of solute (*AAS* or the synthesized Na_2TP) and checking whether it can be dissolved or not. In the other set, the solutions of synthesized disodium terephthalate were also mixed with various amounts of water and MEG in order to produce different ternary solutions of $\text{Na}_2\text{TP} + \text{MEG} + \text{H}_2\text{O}$. In the end, samples from prepared solutions, one by one, were loaded in temperature analysis experimental setup and the freezing points were determined. During the temperature analysis, the temperature of the samples was reduced gradually. As described in Fosbøl *et al.*¹⁶, when the first ice crystals are formed, energy is released according to the following reaction (Rec. 2):



This energy, the latent heat of fusion of water, increases the temperature of the solution and after that; the ice formation can be registered. The variation of the temperature as a function of time is depicted in Figure 1. When crystals appeared in this process and the temperature was close to the freezing point, a plateau was observed, indicated by "A" in Figure 1. After the plateau, the temperature had a slight down sloping trend because the formation of ice changed the water concentration in the liquid phase. The maximum of the plateau was the freezing point temperature. When an apparent plateau was observed, over approximately 30 seconds to 1 minute, the sample was gently heated up until crystals visually disappeared from the solution. If the solution was overheated, the seeds would also disappear and the following data would be less accurate. It was therefore vital not to heat too much. After this process, the sample was further cooled in order to repeat the cycle and create a second plateau, which denoted the second experimental point. The experiment was repeated at least five times, and

the average temperature was taken to be the freezing point of the specific sample. Figure 1 shows three consecutive observations of the freezing point over a time interval of 400 seconds.

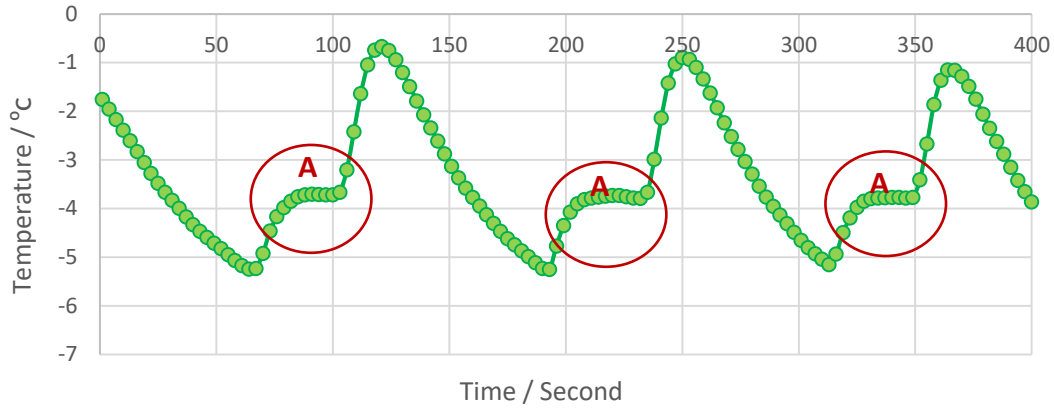


Figure 1, A snapshot of temperature analysis recording figure

2.3.2. Gravimetric experiments

Mixtures with an excess amount of solute (AAS) in various binary solvents of water and ethylene glycol ($H_2O + MEG$), and ternary mixtures of sodium hydroxide, water and ethylene glycol ($H_2O + MEG + NaOH$) were prepared. The containers of mixtures were placed in a thermal bath kept at 25 °C and agitated for 24 hours in order to be saturated with Na_2TP and $NaOH$. Sodium hydroxide is highly soluble in water and aqueous mixtures. The solubility of $NaOH$ in water is 51.8 mass % at 20 °C.¹⁹ Therefore and considering the proportion of AAS and water, we assumed that all $NaOH$ was dissolved in the solvent. Thus, in the mixtures, the mass of $NaOH$ ($m_{NaOH@solution}$) in g , the $NaOH$ mole numbers (n_{NaOH}), and its molality ($b_{NaOH@solution}$) was obtained through following equations (Eq. 1 to Eq. 3).

$$m_{NaOH@solution} = m_{NaOH@solvent} + w_{NaOH@AAS} * m_{AAS} \quad Eq. 1$$

$$n_{NaOH} = \frac{m_{NaOH@solution}}{MW_{NaOH}} \quad Eq. 2$$

$$b_{NaOH@solution} = \frac{n_{NaOH}}{m_{H_2O}/1000} \quad Eq. 3$$

$m_{NaOH@solvent}$ is the mass of $NaOH$ in the solvent in g , $w_{NaOH@AAS}$ is the mass fraction of $NaOH$ in AAS, m_{AAS} and m_{H_2O} are the masses of the AAS and solvent in g respectively, and MW_{NaOH} is the molar mass of $NaOH$ (g/mol). We expressed the molality (b) as mole solute/kg water.

The solutions were filtered at 25 °C and samples collected in Büchner flasks, as described in Murcia *et al.*¹⁷. Then samples were weighed and heated to 230 °C for 24 hours in order to evaporate all H_2O and MEG leaving only Na_2TP and $NaOH$. Finally, after complete drying, solids were cooled in a desiccator and weighed again. The molality of $NaOH$ in the initial solution and the samples were the same, therefore the mass of $NaOH$ in the residues ($m_{NaOH@residues}$) in g could be calculated by this equation (Eq. 4):

$$m_{NaOH@residues} = m_{H_2O@sample} * 10^{-3} * b_{NaOH} * MW_{NaOH} \quad Eq. 4$$

$m_{H_2O@sample}$ is the mass of water in the sample (g), which is the difference in the mass of sample and mass of residues (g). The mass of Na_2TP in g at the residues was calculated by following equation (Eq. 5):

$$m_{Na_2TP@residues} = m_{residues} - m_{NaOH@residues} \quad Eq. 5$$

Equation number 6 was used for calculating the solubility of Na_2TP or its saturation weight percent.

$$m\% Na_2TP = \frac{m_{Na_2TP@residues}}{m_{sample}} * 100 \quad Eq. 6$$

These gravimetry experiments were repeated at 40 °C, 50 °C, 60 °C, and 70 °C.

2.3.3. Titration experiments

Similar to the gravimetric method described above, saturated solutions were prepared at 25 °C. Due to the high solubility of $NaOH$, it was assumed that all the $NaOH$ content of the AAS was dissolved in the solvent. As a result, the number of mole ($n_{NaOH@solution}$) and the molality (b_{NaOH}) of $NaOH$ in solution was calculated from Eq. 7 and Eq. 8:

$$n_{NaOH@solution} = \frac{w_{NaOH@AAS} * m_{AAS}}{MW_{NaOH}} \quad Eq. 7$$

$$b_{NaOH} = \frac{n_{NaOH@solution}}{m_{H_2O@solution} / 1000} \quad Eq. 8$$

MW_{NaOH} is the molar mass of $NaOH$ (g/mol), m_{AAS} is the mass of AAS added to the solution (g), $w_{NaOH@AAS}$ is the mass fraction of $NaOH$ at AAS and $m_{H_2O@sample}$ is the mass of water in the sample (g).

Syringes and syringe filters were kept at the same temperature in Heraeus incubator. The samples were collected from their containers by these syringes with syringe filters. Then, samples were weighed and diluted with deionized water. After that, all samples were titrated following the Fosbøl *et al.*¹⁸ procedure. The number of Na^+ moles in each sample ($n_{Na^+@sample}$) could be obtained from titration results and Eq. 9.

$$n_{Na^+@sample} = C_{HCL} * V_{HCL} \quad Eq. 9$$

C_{HCL} is the molarity ($mole/liter$) and V_{HCL} is the total volume ($liter$) of the HCl titrant used to reach the last equivalent point, abbreviated as "EP" (indicating the termination of Rec. 6). The mass of the water in each sample ($m_{H_2O@sample}$) was needed to calculate the Na_2TP solubility and it could be found from Eq. 10:

$$m_{H_2O@sample} = \frac{m_{sample} - (0.5 * MW_{Na_2TP} * n_{Na^+@sample})}{1 + (b_{NaOH} * MW_{NaOH}) - (0.5 * MW_{Na_2TP} * b_{NaOH})} \quad Eq. 10$$

m_{sample} is the total mass of the sample (g). MW_{Na_2TP} and MW_{NaOH} are the molar masses of the Na_2TP and $NaOH$ respectively (g/mol).

The following relation (Eq. 11) provided us the mass of $NaOH$ in g, indicated by $m_{NaOH@sample}$, in samples.

$$m_{NaOH@sample} = m_{liq@sample} * b_{NaOH} * MW_{NaOH} \quad Eq. 11$$

Finally, the mass of Na_2TP ($m_{Na_2TP@sample}$) in g could be estimated by Eq. 12 and Eq. 13 gave the mass percent of Na_2TP ($m\% Na_2TP$) or its solubility in each sample.

$$m_{Na_2TP@sample} = m_{sample} - m_{H_2O@sample} - m_{NaOH@sample} \quad Eq. 12$$

$$m\% Na_2TP = \frac{m_{Na_2TP@sample}}{m_{sample}} * 100 \quad Eq. 13$$

In addition to 25 °C, these experiments were also conducted at 40 °C, 50 °C, and 60 °C.

AAS dissolves in water according to the following reaction:



As indicated in Figure 2, due to the presence of $NaOH$, dissolving AAS in water led to a quite high pH (approximately 12). Na_2TP is the conjugated base of H_2TP just like any other similar organic base (e.g. sodium acetate). The formed TP^{2-} is a di-protic base having the following reactions:



The acid dissociation constants (Rec. 5 and Rec. 6) were estimated through various theoretical and experimental methods and have been reported in previously published studies. Some of these studies are listed in Table 3.

Table 3, Experimental and theoretical pK_a values reported in the literature

Reference	Title	pK_{a1}	pK_{a2}	Method	Type
Gluck et al. ²⁰	Determination of acidity constants of monoprotic and diprotic acids by capillary electrophoresis	3.25	4.51	Capillary electrophoresis	Semi-empirical
Wroński ²¹	Fingerprint of anions involving pKa, mobility and concentration established by using capillary isotachophoresis	-	4.48	isotachophoresis technique	experimental
Cerar and Podlipnik ²²	Relationships Between Aqueous Acidities of Benzene Polycarboxylic Acids and Computed Surface-electrostatic Potentials and Charges	3.32	4.56	MARVIN cheminformatics software developed by ChemAxon (2008)	Theoretical
Park and Sheehan ²³	Phthalic acids and other benzenepolycarboxylic acids	3.54	4.46	Unknown	statement

Tummanapelli and Vasudevan ²⁵	Estimating successive pKa values of polyprotic	3.51	4.82	ab initio Car–Parrinello molecular dynamics simulations in conjunction with meta-dynamics calculations	Theoretical
Guillory ²⁶	CRC Handbook of Chemistry and Physics	3.54	4.46	Unknown	statement

Tummanapelli and Vasudevan²⁵ compared their modeling results with experimental data referring to Maxwell and Partington (1937)²⁷. Also Braude and Nachod²⁸ referred to experimental values by Maxwell and Partington (1937)²⁷. Maxwell and Partington (1937)²⁷ measured the pKa values of a series of similar polybasic acids. They did not measure the pK_a s of terephthalic acid. According to Maxwell and Partington (1936)²⁹, the extremely slight solubility of this acid made it impossible to measure its pK_a values.

Since the pK_a values reported by Sheehan⁸ were in close agreement with experimental and theoretical values reported in the literature (Table 3), we also applied those numbers for our study. The values of the equilibrium constants of terephthalic acid dissociation reactions (*Rec. 5* and *Rec. 6*) are close together, and we could not detect the equivalent point of second dissociation reaction (*Rec. 5*) in this experimental study. Therefore, the titration curve in Figure 2 only shows one equivalent point at about pH 3.5 relating to the completion of the first dissociation reaction (*Rec. 6*); the termination of *Rec. 5* was not detectable in our titration experiments. However, our titration curves of AAS aqueous solutions had two equivalence points as seen in Figure 2. The first equivalence point is near pH 8 and the second around pH 3.5. The first equivalence point reflects the reaction with *NaOH* (*Rec. 7*), and the second refers to *Rec. 5* and *Rec. 6* combined. The two reactions are indistinguishable during titration.



The interpretation of the experiments is very similar to previous work by Fosbøl *et al.*³⁰.

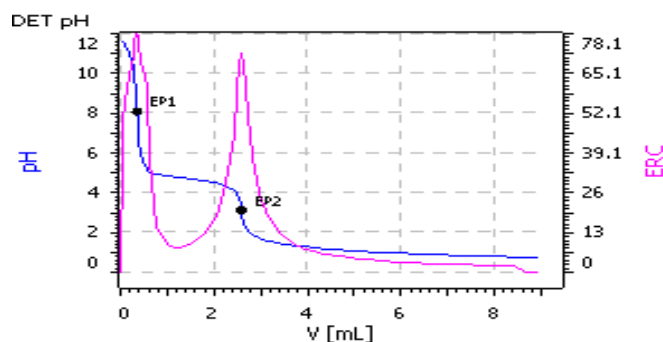


Figure 2, Titration curve for aqueous Na_2TP solution at 25°C. The blue line is the pH curve and the pink line is the derivative ($d\text{pH}/dV$) of the titration curve, referred to as Endpoint Recognition Criteria (ERC)

2.4. Uncertainty and deviation

All the experiments were repeated at least three times having standard deviations of less than 0.05 except 10 points (see Table 4 to 6 in the next section). Temperature analysis experiments were repeated at least five times and the standard deviations are presented in Table 7 and 8. Typical standard deviations are in the order of 0.03 °C or lower.

3. Results and Discussion

Table 4 presents the Solid Liquid Equilibrium (SLE) data of quaternary system of Na_2TP , $NaOH$, H_2O , and MEG . The data are the results of titration experiments on AAS in different solvent mixtures of H_2O , and MEG . The solid phase is Na_2TP in all the data points of Table 4.

Table 4, SLE results from titration experiments on AAS in various solvents of $MEG + H_2O$ at atmospheric condition. Column 1 and 2 give the solubility of the same component in two different units – for the ease of comparison.

weight percent of Na_2TP	molality of Na_2TP	molality of $NaOH$	molality of MEG	t	Standard uncertainties	Type Solid
$100 * \frac{g_{Na_2TP}}{g_{total}}$	$\frac{mole}{kg\ water}$	$\frac{mole}{kg\ water}$	$\frac{mole}{kg\ water}$	$^{\circ}C$	u	
13.11%	0.7251	0.2440	0	25	0.02	Na_2TP
6.53%	0.6221	0.1874	13.8889	25	0.01	Na_2TP
4.19%	0.6896	0.2901	37.0370	25	0.02	Na_2TP
3.08%	0.9351	0.3294	83.3333	25	0.03	Na_2TP
12.95%	0.7142	0.2080	0	40	0.01	Na_2TP
6.52%	0.6216	0.2348	13.8889	40	0.00	Na_2TP
3.89%	0.6370	0.2794	37.0370	40	0.01	Na_2TP
2.87%	0.8709	0.5211	83.3333	40	0.03	Na_2TP
2.17%	3.3919	2.3706	500	40	0.11	Na_2TP
12.37%	0.6793	0.2790	0	50	0.00	Na_2TP
6.63%	0.6318	0.2130	13.8889	50	0.03	Na_2TP
3.87%	0.6348	0.2483	37.0370	50	0.01	Na_2TP
2.87%	0.8712	0.3953	83.3333	50	0.02	Na_2TP
2.13%	3.3258	1.8011	500	50	0.09	Na_2TP
12.76%	0.7029	0.2443	0	60	0.01	Na_2TP
6.60%	0.6302	0.3213	13.8889	60	0.02	Na_2TP
3.97%	0.6513	0.3319	37.0370	60	0.03	Na_2TP
2.76%	0.8365	0.5270	83.3333	60	0.01	Na_2TP
2.18%	3.4101	2.3759	500	60	0.48	Na_2TP

The results of the gravimetric experiments on quaternary system of Na_2TP , $NaOH$, H_2O , and MEG are given in Table 5 and 6. Table 5 includes the solubility data of AAS in various solvent mixtures of water and MEG . We also examined the effect of excess $NaOH$ on the solubility of AAS by gravimetric experiments. The results of these examinations are reported in Table 6. The solid phases in both Table 5 and 6 are disodium terephthalate.

Table 5, SLE results from gravimetric experiments on AAS in various solvents of MEG + H₂O at atmospheric condition. Column 1 and 2 give the solubility of Na₂TP in two different units for the ease of comparison.

weight percent of Na ₂ TP	molality of Na ₂ TP	molality of NaOH	molality of MEG	t	Standard uncertainties	Type Solid
100 * g_{Na_2TP} / g_{total}	mole/kg water	mole/kg water	mole/kg water	°C	u	
12.35%	0.6773	0.2464	0	25	0.00	Na ₂ TP
6.43%	0.6119	0.1966	13.8889	25	0.01	Na ₂ TP
4.18%	0.6877	0.2940	37.0370	25	0.00	Na ₂ TP
3.00%	0.9095	0.3819	83.3333	25	0.00	Na ₂ TP
2.24%	3.5063	2.0688	500	25	0.03	Na ₂ TP
12.22%	0.6697	0.2637	0	40	0.01	Na ₂ TP
6.88%	0.6583	0.2762	13.8889	40	0.05	Na ₂ TP
4.17%	0.6859	0.3495	37.0370	40	0.07	Na ₂ TP
3.14%	0.9576	0.6297	83.3333	40	0.08	Na ₂ TP
2.12%	3.3205	2.8990	500	40	0.97	Na ₂ TP
12.04%	0.6589	0.2872	0	50	0.01	Na ₂ TP
6.92%	0.6624	0.2387	13.8889	50	0.03	Na ₂ TP
4.13%	0.6794	0.3251	37.0370	50	0.06	Na ₂ TP
2.92%	0.8878	0.6517	83.3333	50	0.13	Na ₂ TP
2.21%	3.4584	2.8251	500	50	0.49	Na ₂ TP
12.19%	0.6683	0.2819	0	60	0.00	Na ₂ TP
6.83%	0.6535	0.2896	13.8889	60	0.01	Na ₂ TP
3.79%	0.6227	0.4710	37.0370	60	0.04	Na ₂ TP
2.64%	0.8017	0.7033	83.3333	60	0.01	Na ₂ TP
1.94%	3.0274	3.1297	500	60	0.10	Na ₂ TP
12.13%	0.6652	0.3193	0	70	0.00	Na ₂ TP
6.70%	0.6411	0.3355	13.8889	70	0.00	Na ₂ TP
4.06%	0.6677	0.4963	37.0370	70	0.01	Na ₂ TP
2.82%	0.8568	0.8050	83.3333	70	0.01	Na ₂ TP
1.84%	2.8718	4.3272	500	70	0.04	Na ₂ TP

The determined freezing points for the synthesized Na₂TP in the solutions of H₂O and MEG are shown in Table 7 and depicted in Figure 3. These are the results of temperature analysis experiments on synthesized Na₂TP as explained in subsection 2.1.1. The results of freezing point measurements of solutions of AAS in mixtures of H₂O and MEG are reported in Table 8. Ice, H₂O_(s), is the only solid observed in all temperature analysis experiments of AAS and synthesized Na₂TP.

Table 6, SLE results from gravimetric experiments on AAS in solvents of MEG + H₂O + NaOH at atmospheric condition
 Column 1 and 2 give the solubility of Na₂TP in two different units for the ease of comparison.

weight percent of Na ₂ TP	molality of Na ₂ TP	molality of NaOH	molality of MEG	t	Standard uncertainties	Type Solid
$100 * g_{Na_2TP} / g_{total}$	mole/kg water	mole/kg water	mole/kg water	°C	u	
10.14%	0.5514	0.6560	0	25	0.00	Na ₂ TP
6.07%	0.5928	0.7022	14.4683	25	0.03	Na ₂ TP
4.15%	0.6928	1.0007	37.4511	25	0.03	Na ₂ TP
2.49%	0.7848	1.4641	84.8523	25	0.01	Na ₂ TP
1.89%	3.1905	6.5296	538.8277	25	0.14	Na ₂ TP
9.88%	0.5356	0.6628	0	40	0.00	Na ₂ TP
5.84%	0.5697	0.7734	14.4683	40	0.02	Na ₂ TP
3.73%	0.6196	0.9647	37.4511	40	0.01	Na ₂ TP
2.42%	0.7527	1.4540	84.8523	40	0.03	Na ₂ TP
1.81%	3.0487	6.5492	538.8277	40	0.03	Na ₂ TP
10.02%	0.5451	0.6966	0	60	0.01	Na ₂ TP
5.96%	0.5824	0.8514	14.4683	60	0.03	Na ₂ TP
3.75%	0.6247	1.1294	37.4511	60	0.00	Na ₂ TP
2.43%	0.7572	1.6265	84.8523	60	0.02	Na ₂ TP
1.77%	2.9841	7.7912	538.8277	60	0.23	Na ₂ TP

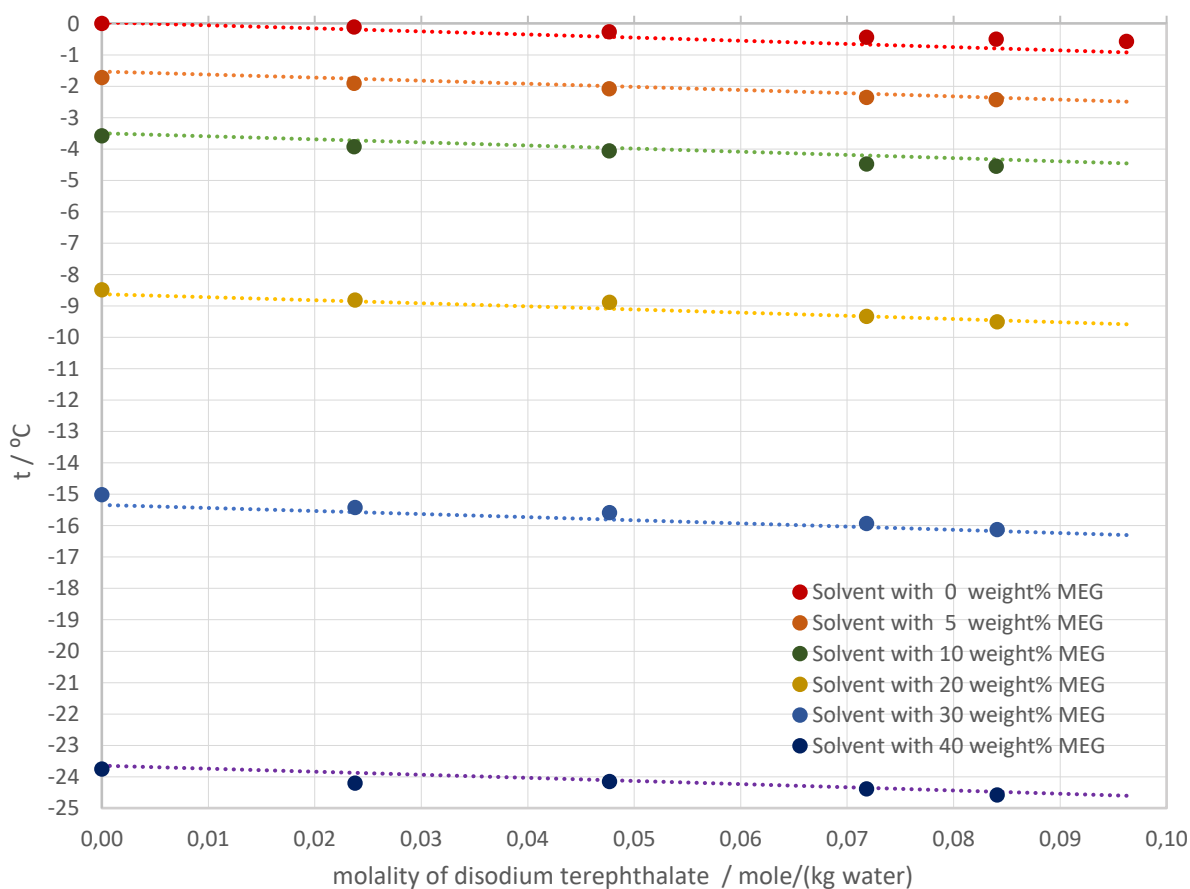


Figure 3, Freezing point results of synthesized Na₂TP in aqueous MEG solutions at atmospheric condition

Table 7, Freezing point results of synthesized Na_2TP in aqueous MEG solutions at atmospheric condition. Column 1 and 2 give the composition of the solutions in two different units for the ease of comparison.

<i>weight percent of Na_2TP</i>	<i>molality of Na_2TP</i>	<i>molality of H_2TP</i>	<i>molality of MEG</i>	<i>t</i>	<i>Standard uncertainties</i>	<i>Type Solid</i>
$100 * \frac{g_{Na_2TP}}{g_{total}}$	<i>mole/kg water</i>	<i>mole/kg water</i>	<i>mole/kg water</i>	$^{\circ}C$	u	
2.00%	0.0962	0.0014	0	-0.566	0.01	Ice
1.75%	0.0840	0.0012	0	-0.499	0.04	Ice
1.66%	0.0840	0.0012	0.8665	-2.430	0.03	Ice
1.57%	0.0840	0.0012	1.8241	-4.547	0.02	Ice
1.40%	0.0841	0.0012	4.1156	-9.502	0.03	Ice
1.23%	0.0841	0.0012	7.0393	-16.125	0.06	Ice
1.05%	0.0841	0.0012	10.9483	-24.586	0.02	Ice
1.50%	0.0718	0.0011	0	-0.437	0.03	Ice
1.43%	0.0718	0.0011	0.8619	-2.353	0.05	Ice
1.35%	0.0718	0.0011	1.8469	-4.479	0.03	Ice
1.20%	0.0718	0.0011	4.1052	-9.334	0.05	Ice
1.05%	0.0718	0.0011	7.1020	-15.930	0.04	Ice
0.90%	0.0718	0.0011	10.8824	-24.394	0.02	Ice
1.00%	0.0477	0.0007	0	-0.268	0.03	Ice
0.95%	0.0477	0.0007	0.8791	-2.084	0.03	Ice
0.90%	0.0477	0.0007	1.8090	-4.061	0.03	Ice
0.80%	0.0477	0.0007	4.0428	-8.890	0.04	Ice
0.70%	0.0477	0.0007	6.9743	-15.584	0.02	Ice
0.60%	0.0477	0.0007	10.8262	-24.155	0.04	Ice
0.50%	0.0237	0.0004	0	-0.114	0.02	Ice
0.47%	0.0237	0.0004	0.8473	-1.905	0.02	Ice
0.45%	0.0237	0.0004	1.7984	-3.922	0.04	Ice
0.40%	0.0238	0.0004	4.0573	-8.815	0.05	Ice
0.35%	0.0238	0.0004	6.9440	-15.421	0.06	Ice
0.30%	0.0238	0.0004	10.7887	-24.211	0.05	Ice

As can be seen from Figure 3, dissolving Na_2TP into the solution decreased the freezing points with an almost linear trend. Overall, the freezing point dropped exponentially with the amount of MEG. In spite of the MEG content in the system, the freezing points had similar declining trends, which indicates that the molecular interaction between water and Na_2TP is independent of the glycol concentration.

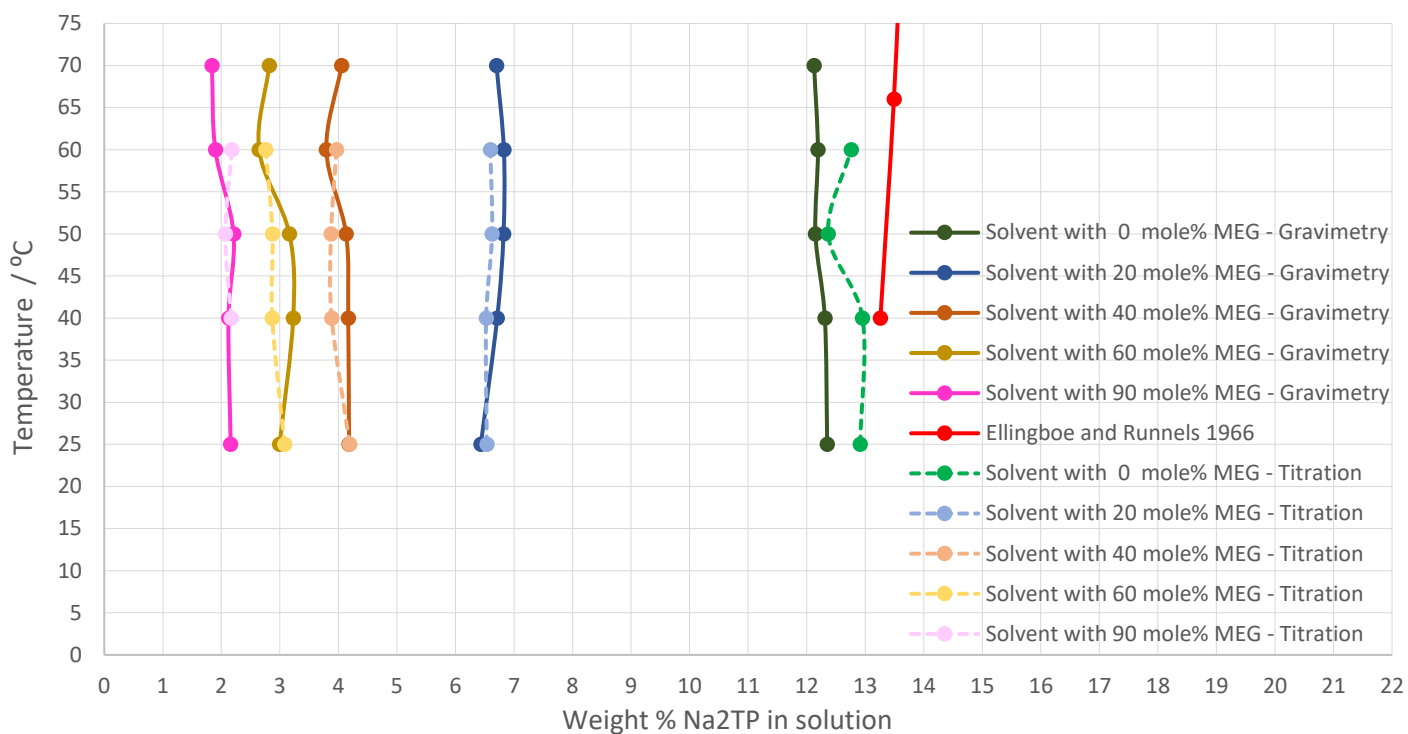


Figure 4, Solubility of disodium terephthalate in solutions of water and ethylene glycol

The solubility of disodium terephthalate in various solutions of water and ethylene glycol as a function of temperature is presented in Figure 4. The data from Table 4 and 5 are plotted in this figure in addition to the only available literature data Ellingboe and Runnels¹³. The Figure 4 does not indicate the content of *NaOH* in the mixture, which is not exactly the same for all data points. This is why a scatter is observed. The accurate data is given in Table 4 and 5. Figure 4 shows that the solutions with a higher concentration of *MEG* have a lower capacity to dissolve *Na₂TP*. The solubility of *Na₂TP* in water is around 13 weight percent. In water containing 20 mole percent *MEG* the solubility of *Na₂TP* is only around 7 weight percent; and this number decreases to around 2 weight percent in a solvent consisting of 90 mole percent *MEG* in water.

In Figure 4, the solubility curve is shown up to 75 °C being only little influenced by temperature. The temperature dependence of disodium terephthalate solubility in both quaternary mixtures (*Na₂TP* + *NaOH* + *H₂O* + *MEG*) and ternary solutions (*Na₂TP* + *NaOH* + *H₂O*) are similar. In both systems, the solubility curves are almost vertical, and the temperature does almost not influence the saturation capacity of the solution.

Overall, *MEG* is influencing the ternary and the quaternary system similarly. Ethylene glycol decreases the solubility of disodium terephthalate in aqueous solutions, but the amount of ethylene glycol does not change the temperature dependency of the solubility curves.

Table 8, Freezing point results of AAS in aqueous MEG solutions at atmospheric condition.
Column 1 and 2 give the composition of the solutions in two different units for the ease of comparison.

weight percent of Na_2TP	molality of Na_2TP	molality of $NaOH$	molality of MEG	t	Standard uncertainties	Type Solid
$100 * \frac{g_{Na_2TP}}{g_{total}}$	mole/kg water	mole/kg water	mole/kg water	°C	u	
1.89%	0.0918	0.0300	0	-0.433	0.02	Ice
3.76%	0.1866	0.0611	0	-0.902	0.05	Ice
5.65%	0.2860	0.0935	0	-1.453	0.05	Ice
7.54%	0.3899	0.1276	0	-2.203	0.03	Ice
9.36%	0.4945	0.1618	0	-2.731	0.04	Ice
10.38%	0.5555	0.1817	0	-3.033	0.05	Ice
11.29%	0.6107	0.1998	0	-3.230	0.02	Ice
1.88%	0.1014	0.0332	1.7901	-3.814	0.05	Ice
3.81%	0.2101	0.0687	1.7901	-4.428	0.04	Ice
5.68%	0.3197	0.1046	1.7901	-5.136	0.03	Ice
7.55%	0.4343	0.1421	1.7901	-5.925	0.08	Ice
9.39%	0.5514	0.1804	1.7901	-6.401	0.05	Ice
1.90%	0.1156	0.0378	4.0277	-8.744	0.03	Ice
3.78%	0.2344	0.0767	4.0277	-9.158	0.20	Ice
5.65%	0.3573	0.1169	4.0277	-9.713	0.05	Ice
7.52%	0.4865	0.1592	4.0277	-10.251	0.05	Ice
9.41%	0.6218	0.2034	4.0277	-11.771	0.04	Ice
1.89%	0.1310	0.0429	6.9046	-14.376	0.02	Ice
3.76%	0.2662	0.0871	6.9046	-15.193	0.04	Ice
5.64%	0.4082	0.1335	6.9046	-16.172	0.02	Ice
7.54%	0.5573	0.1823	6.9046	-16.616	0.04	Ice
1.90%	0.1539	0.0503	10.7406	-23.857	0.03	Ice
3.78%	0.3121	0.1021	10.7406	-24.944	0.01	Ice
5.65%	0.4770	0.1561	10.7406	-25.589	0.05	Ice

The Solid-Liquid Equilibrium diagram for $AAS + H_2O$ is outlined in Figure 5. In this Figure, surprisingly, it can be seen surprisingly, the measured solubility of AAS from our study coincides with the Na_2TP solubility reported by Ellingboe and Runnels¹³. Apparently, AAS , which is a mixture of $NaOH$ and Na_2TP , has similar solubility to the solubility Ellingboe and Runnels¹³ reported for pure Na_2TP .

Ellingboe and Runnels¹³ declared that the solubility of pure Na_2TP in water correspond to the three yellow diamonds in Figure 5. Nonetheless, we found that AAS , which is a mixture of Na_2TP and $NaOH$, has this solubility in pure water. This difference might be caused by the procedure by which Ellingboe and Runnels¹³ produced the Na_2TP . They mixed H_2TP with 10% excess amount of $NaOH$ in water without dissolving the substances completely, and then they removed the product (Na_2TP) which was not dissolved in water, by filtration. Through this manufacturing procedure there is a high risk of trapping $NaOH$ during the crystallization of Na_2TP . Consequently, in spite of washing the Na_2TP one or two times, there is a high risk of contamination of $NaOH$ with produced Na_2TP .

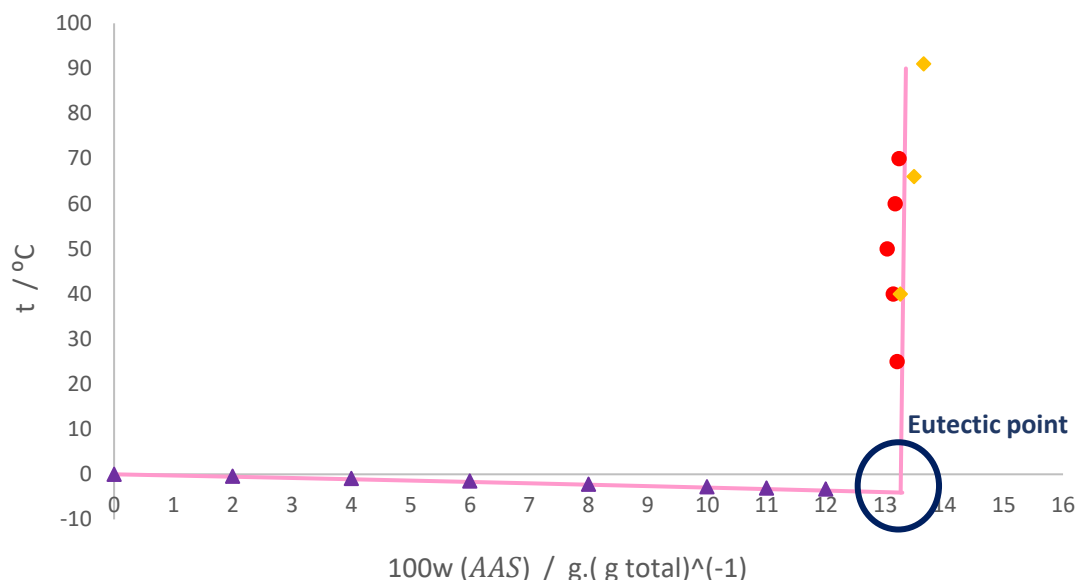


Figure 5, pink line, —, SLE curve of AAS in pure water;
 Yellow diamond, ◆, results of Ellingboe and Runnels 1966¹³ for Pure water;
 Red circle, ●, gravimetry results of AAS in pure water;
 Purple triangle, ▲, temperature analysis Result for pure water

However in agreement with Ellingboe and Runnels¹³, we also observed that temperature changes, higher than the eutectic temperature, have very little effect on the solubility of Na_2TP in water (Figure 4 and 5). Thus, the equilibrium constant (K_{eq}) of dissociation reaction of disodium terephthalate (Rec.3) appears almost constant and it is not a noticeable function of temperature. Therefore, based on the Van't Hoff equation (Eq. 14), the heat (ΔH_{rxn}) of this salt dissolution reaction (Rec.3) can be near to zero. This indicates that the formation enthalpy of the solid $\Delta_f H_{Na_2TP(s)}^o$ is quite close to the enthalpy formation of $2\Delta_f H_{Na^+}^o + \Delta_f H_{TP^{2-}}^o$.

$$\frac{d \ln K_{eq}}{dT} = \frac{\Delta H_{rxn}}{RT^2} \quad \text{Eq. 14}$$

R is the gas constant. T is the Kelvin temperature.

The melting point of Na_2TP was also investigated but it was higher than the temperature limit of the applied equipment (340 °C), therefore we could not determine that.

Dissolving disodium terephthalate in water, either in the form of AAS having impurity of $NaOH$ or making the synthesized Na_2TP having minute impurity of H_2TP , was time-consuming and took up to 24 hours. During sample preparation, it was noticed that some solute still existed in the solution undissolved after 8 hours. However, continuous shaking could make it disappear completely after 12 hours. This phenomenon along with the high melting point shows that Na_2TP , similar to H_2TP , has significantly stable solid crystals, durable to thermal energy and unwilling to be dissociated in aqueous solvents.

4. Conclusion

In this work, the solubility of disodium terephthalate in ternary mixtures of $Na_2TP + H_2O + NaOH$, and quaternary solutions of $Na_2TP + H_2O + MEG + NaOH$ were measured at atmospheric condition up to 70 °C. The investigations were performed by gravimetry and titration experimental methods. The results were compared with existing data from Ellingboe and Runnels¹³, and our data are in agreement with previously reported data. For the first time, we present data for the solubility of disodium terephthalate in aqueous solutions of ethylene glycol and sodium hydroxide. The conclusion is that temperature does not have a considerable effect on the solubility of disodium terephthalate. Both ethylene glycol and sodium hydroxide reduce the solubility of Na_2TP . Ethylene glycol does not change the temperature dependency shape of the solubility curve.

The freezing point temperatures were determined by temperature analysis experiments. The ternary solution of $Na_2TP + H_2O + MEG$ and quaternary mixtures of $Na_2TP + H_2O + MEG + NaOH$ were explored. Freezing points in these systems containing Na_2TP , are significantly influenced by temperature. Addition of ethylene glycol reduces the freezing point temperatures significantly. *MEG* cannot alter the slope of the freezing point curves versus composition of disodium terephthalate and the curve has similar slope in all composition of ethylene glycol.

The data produced in this work may contribute to the design of sustainable processes for regeneration and re-use of PET plastic materials contributing thus to the UN sustainability goals. The data have a potential for application in process modeling, which can lead to an optimization of PET chemical recycling processes.

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