Determination of green solvents' water activity by inference of freezing point depression

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Abstract. Deep eutectic solvents (DESs) are novel green solvents with great potential in many industrial applications. Due to their high tunability, DESs can be synthesized and prepared into various concentrations by dilution with water. This work revolutionises the determination of selected DESs' water activity using inferencing their respective freezing point depression. Using the Hildebrand-Scott equation, the freezing point depression of the respective DESs in various concentrations is then correlated to the water activity. This inferential correlation provides an alternate but convenient way of determining a solution's water activity in absence of a water activity meter. The highest freezing point depression of almost -10 °C was observed on the choline chloride and ethylene glycol in 1:2 molar ratio DES at 50 wt% concentration, with corresponding water activity determined at 0.909.

Introduction

In the interest of sustainability, there has been growing interest around the world in the search for green solvents. An effective solvent not only acts as a key enabler in chemical processes, but the sustainability framework also prescribes the solvent to comply with major assessment criteria, ranging from conformance to green chemistry principles, the satisfaction of life cycle evaluations, as well as fulfilment of the "10R Framework" such as recycle, reuse, reduce etc associated with the modern circularity philosophy [1].

Deep eutectic solvents (DESs) of late have been classified as green alternatives to molecular solvents and ionic liquids (ILs) [2]. They are characterised as eutectic mixtures formed between quaternary ammonium, phosphonium or sulfonium salts and hydrogen bond donors (HBDs) with a freezing temperature lower than their respective individual components. Marcus [3] concluded that DESs have the advantage over other conventional industrial solvents in that they are relatively easy to be synthesised and highly tunable. Their synthesis ingredients are also easily available. Most importantly, the synthesis and production of these green solvents are highly cost-competitive, through relatively benign processes which support the sustainability framework compared to other common industrial organic solvents [4].

Deep Eutectic Solvents

A eutectic system is a mixture of chemical compounds or elements that demonstrates a single and homogenous chemical composition which freezes at a significantly lower temperature than its forming components [5]. The term DESs has been specified mainly to differentiate them from

authentic ionic liquids (ILs) in light of different characteristics in some solvent properties, and the fact that some DES components are non-ionic.　The great freezing point depression exhibited by the eutectic mixture does not occur in ILs but only in DESs as a unique form of change in the solvent's physical property.　Abbot et al. noted that the freezing point depression of DESs can be as high as hundreds of degrees Celsius relative to its components [6].

DESs have a wide range of industrial applications with established performance. Fourmentin, Costa Gomes [7] presented several successful cases using DESs in innovative medical and pharmaceutical formulations in enhancing selective drugs' bioavailability.　There are also growing interests in DESs for biomass treatments, metal processing, separation and extraction for pharmaceutical and medical applications.　DESs have also been studied by Zhou et al. with prospective findings that when used as novel reaction mediums, they will help to improve enzymatic activity stabilization in the fields of bio-catalysis [8]. DESs have also been proven to offer cost-effective, reliable and efficient performance for CO_2 capture with excellent regeneration capacity [9].　Specific to the oil and gas industry, DESs have been identified as potential greener and more cost-effective alternatives compared to conventional surfactants in improving enhanced oil recovery (EOR) in the exploration and production of heavy oils [10, 11].

Selection and Synthesis of DESs and Derivatives
DESs are broadly classified into four categories depending on the nature and properties of the mixing components [12].　In this work, the focus is given on a few DES species from DES III, IV and the novel type DES V (also known as natural DES, or NADES) [13].　Table 1 below lists the classification of various conventional DES types, along with the general formula.

Table 1: Conventional DES classifications with general formula. [3]

Type	General Formula
I (quarternary salt + metal halide)	$Cat^+X^-zMCl_x$
II (quarternary salt + hydrated metal halide)	$Cat^+X^-zMCl_x \cdot yH2O$
III (quarternary salt + HBD)	Cat^+X^-zRZ
IV (metal halide + HBD)	$MCl_x^+RZ = MCl_{x-1}+\cdot RZ+MCl_{x+1}$

Fifteen DESs of various concentrations have been synthesized and are subject to freezing point depression measurement.　The list of DESs prepared in this work is listed in Table 1 below, along with the respective Hydrogen Bond Acceptor (HBA) and Hydrogen Bond Donor(s) (HBDs) and their respective corresponding molar composition in each DES specimen.

Table 2: List of DESs in various concentrations synthesised for water activity determination.

DES ID	Description and Concentration	HBA: HBD molar composition
1	DES IIIa 2 wt%	choline chloride: ethylene glycol 1:2
2	DES IIIa 5 wt%	As above
3	DES IIIa 10 wt%	As above
4	DES IIIa 20 wt%	As above
5	DES IIIa 50 wt%	As above
6	DES IIIb 10 wt%	choline chloride: glycerol 1:2
7	DES IIIc 10 wt%	choline chloride: urea: glycerol 1:1:1
8	DES IIId 10 wt%	choline chloride: levulinic acid 1:2
9	DES IV 10 wt%	zinc chloride: ethylene glycol 1:4
10	DES V 10 wt% solubilised in Polysorbate 20	thymol: coumarin 2:1
11	DES V 10 wt% solubilised in Poly Suga Mulse	As above
12	DES Va 10 wt% solubilised in Polysorbate 20	thymol: coumarin: ethylene glycol 2:1:2
13	DES Va 10 wt% solubilised in Poly Suga Mulse	As above
14	DES Vb 10 wt% solubilised in Polysorbate 20	thymol: coumarin: glycerol 2:1:1
15	DES Vb 10 wt% solubilised in Poly Suga Mulse	As above

Water Activity

Water activity (a_w) of a solution is the ratio between the solution vapour pressure alone when subject to a completely undisturbed balance with the surrounding air media, and the vapour pressure of distilled water under an identical condition. A water activity of 0.90 means the vapour pressure is 90% of that of pure water. Water activity increases with higher temperatures. Mathematically, water activity (a_w) is defined as:

$$a_w = \frac{p}{p_0}$$

Eq. 1

of which $a_w =$ water activity of solvent
          $p =$ vapour pressure of the solvent
          $p_0 =$ vapour pressure of pure water

Water activity is important in the evaluation of salting out effects of any aqueous two-phase system (ATPS). In addition, water activity also enables the determination of other critical thermodynamic properties of the solution, such as the solvent's vapour pressure and osmotic coefficients. [14]. The water activity of a solvent can be measured directly using an industrial-scale water activity meter. Alternately, water activity can be determined through experiments, and compared against the various Non-random Two Liquid (NTRL) models and derivatives available to examine the measured water activity accuracy [15]. The resultant water activity data can be utilised to assess the solute-solvent interactions and behaviours in an array of water activity and vapour pressure data.

This work prescribes an alternate empirical method using simple and easily available laboratory apparatus, to determine the DESs' water activity in absence of an industrial-scale water activity meter.

Experimental Procedures

The DESs freezing point depression is measured using a modified and simplified inflected temperature method adopted by Haghighi et al. [16]. This method requires a temperature bath for cooling control, thermometers to measure temperatures of the solution as well as the reference liquid, which in this case is ethylene glycol. For this work, the Pour and Cloud Point Apparatus (Model: Anton-Parr) is used to provide temperature bath control. The experimental setup is represented in Figure 1 below.
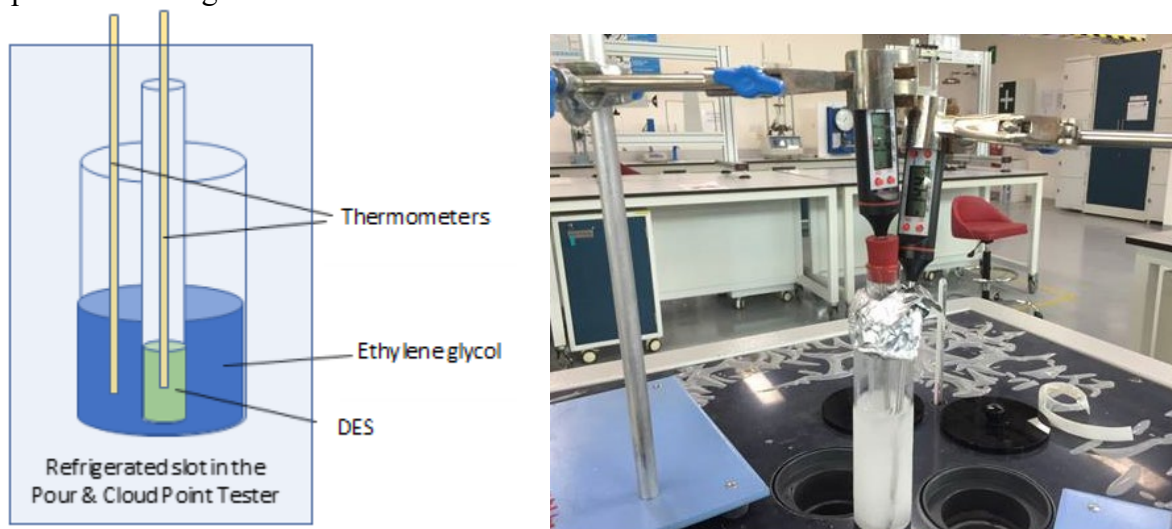
Fig. 1: Schematic and picture of the DES freezing point depression setup. The container was retracted from the refrigerated slot for a better illustration shown in the picture.

The Cloud and Pour Point Tester temperature control was set to 5°C. Upon temperature stabilisation, the Pour Point Tester container filled with 20-ml reference liquid i.e. ethylene glycol, and the test tube filled with 5-ml DES specimen were lowered down to the refrigerated slot. Both the reference liquid and DES specimen were installed with separate digital thermometers to record the respective temperature readings. The temperature control was set by reducing the refrigerated slot of the Cloud and Pour Tester gradually until such time that the temperature of the DES specimen increased upon reaching its freezing point. This phenomenon is indicated by a corresponding increase in the test tube content absolute temperature following the liberation of the exotherm from the DES specimen upon reaching its freezing point.

The experiment was then continued by adjusting the Cloud and Pour Point temperature control continuously with reducing temperature set point until such time that the absolute temperatures in both the reference liquid and DES specimen reached parity. When this was achieved, the Cloud and Pour Point Tester temperature control was reset to 5 °C and both thermometer readings were recorded every minute. A differential temperature plot between the reference liquid and DES specimen ($T_{DES} - T_{ref}$) was generated. The point of which an inflection on the differential temperature plot occurred corresponded with the inferred freezing point depression (ΔT_f) of the DES specimen.

Results and Discussions

Figure 2 below provided an example of an inflection temperature run on DES IIIa of 20 wt% concentration.
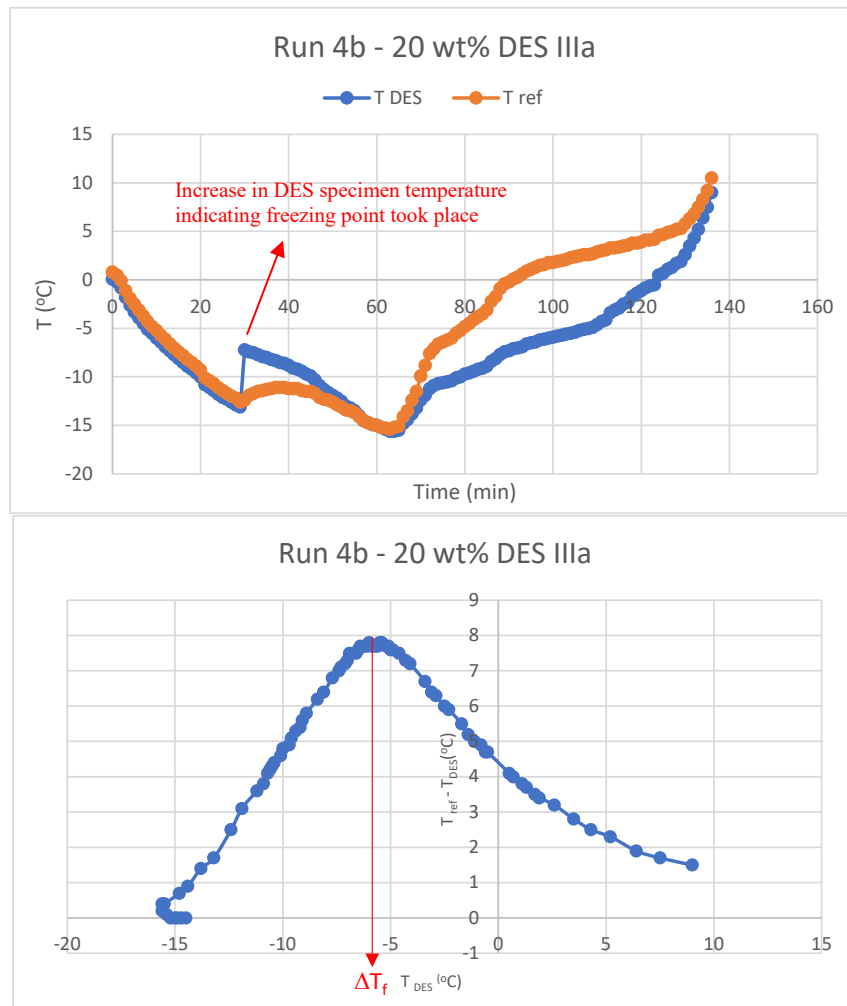
Fig. 2: (a) Absolute temperature plot, and (b) differential temperatures vs T_{DES} plot for DES IIIa 20wt%

From Figure 2(b) above, the inflection point occurred at T_{DES} = –5.3°C.   This point signified the freezing point depression (ΔT_f) of the DES specimen tested in the experimental run.   With this freezing point depression ascertained, the DES specimen freezing point (T_f) relative to 273.15K could then be calculated. Using Hildebrand & Scott's equation similar to previous studies, the respective DES specimen water activity could then be determined [17].

$$\ln a_w = \frac{-\Delta H_f}{R} \frac{(T_f - T)}{T_f T} + \frac{\Delta C_f}{R} \left[\frac{(T_f - T)}{T} - ln\left(\frac{T_f}{T}\right) \right] \qquad \text{Eq. 2}$$

of which T is the DES specimen freezing point in K, T_f signifies the water freezing point in K, ΔH is the latent heat of water which is 6,088 J/K/mol, ΔC_f is the change of specific heat of water equals 38.7 J/K/mol and R is the gas constant.

Table 3 below summarized the inference water activity of all DES specimens examined using the inflection temperature method.

From the runs generated, a higher concentration of the same DES yielded greater freezing point depression, which in return resulted in lower water activity. In terms of DESs III and IV at 10 wt% concentration, their empirical water activity appeared to be within the range between 0.97 and

0.98. For NADES DES V solubilized in either solubilizer of Polysorbate 20 and Poly Suga Mulse (PSM), the resultant freezing point depression of all these solutions yielded insignificant difference, with a corresponding water activity in the range of 0.95 to 0.96.

Table 3: Summary of freezing point depression and calculated water activity of the various DES specimens.

DES ID	Description and Concentration	Freezing Point Depression, ΔT_f (K)	Freezing Point, T_f (K)	Ln a_w	Water Activity, a_w
1	DES IIIa 2 wt%	-0.2	272.95	-0.0019	0.998
2	DES IIIa 5 wt%	-0.8	272.35	-0.0078	0.992
3	DES IIIa 10 wt%	-3.2	269.95	-0.0310	0.969
4	DES IIIa 20 wt%	-6.0	267.20	-0.0578	0.944
5	DES IIIa 50 wt%	-9.8	263.35	-0.0953	0.909
6	DES IIIb 10 wt%	-1.9	271.25	-0.0184	0.982
7	DES IIIc 10 wt%	-3.1	270.05	-0.0301	0.970
8	DES IIId 10 wt%	-2.2	270.95	-0.0213	0.979
9	DES IV 10 wt%	-3.4	269.75	-0.0330	0.968
10	DES V P20 10 wt%	-4.9	268.25	-0.0476	0.954
11	DES V PSM 10 wt%	-5.1	268.05	-0.0495	0.952
12	DES V(a) P20 10 wt%	-5.3	267.85	-0.0514	0.950
13	DES V(a) PSM 10 wt%	-4.5	268.65	-0.0437	0.957
14	DES V(b) P20 10 wt%	-4.6	268.55	-0.0446	0.956
15	DES V(b) PSM 10 wt%	-4.4	268.75	-0.0427	0.958

Conclusions

The water activity of the various DES specimens can be inferenced by determining its freezing point depression following the inflected temperature procedures. The experimental setup is relatively hassle-free using common equipment available in most research laboratories, and most importantly cost-effective relative to the investment in procuring a water activity meter.   Further works may involve a comparison of the inference water activity values against measurements using industrial water activity meter, to determine the precision of such an inference method. The inference results can also be compared against modelling output, as a means for calibrating the model accuracy.

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