ELSEVIER

Contents lists available at ScienceDirect

# Microchemical Journal

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





# Remarks on use of the term "deep eutectic solvent" in analytical chemistry

Vasil Andruch <sup>a,\*</sup>, Patrycja Makoś-Chełstowska <sup>b</sup>, Justyna Płotka-Wasylka <sup>c,d,\*</sup>

- a Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, P. J. Safárik University, Košice, Slovakia
- b Department of Process Engineering and Chemical Technology, Faculty of Chemistry, Gdansk University of Technology, Poland
- <sup>c</sup> Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 80-233 Gdańsk, Poland
- <sup>d</sup> BioTechMed Center, Gdańsk University of Technology, 80-233 Gdańsk, Poland

#### ABSTRACT

About 20 years ago, Abbott and co-workers researched new solvents that were based on mixtures of choline chloride with urea and carboxylic acids and that were liquid at ambient temperature. The term "deep eutectic solvent" (DES) was later adopted for similar mixtures. As DESs have a number of interesting features, they quickly attracted the attention of researchers and found application in various branches of chemical and materials research. To date, various definitions of DES have been proposed. Nevertheless, there are still differing views among researchers on what a DES really is and what exact properties a mixture must have in order to be included into this group. The prefix "deep" should only be used for deep eutectic solvents with melting points significantly below ideal predictions. Otherwise, the simpler term "eutectic solvent" (ES) should be used. It therefore follows that in order to correctly assign a solvent to the DES or ES group, a phase diagram must be available to evaluate the deviation from the ideality, as well as to quantify the DES's liquid window. The term DES is now commonly used in analytical chemistry, but authors rarely go into a detailed examination of a DES from the viewpoint of whether it actually is a DES or an ES. Instead, they logically focus mainly on the analytical part, that is, on taking advantage of the benefits that the DES provides. Therefore, it may happen that the solvent used is designated as a DES, even if it does not meet all the necessary requirements. Of course, we cannot or should not expect analytical chemists to do a detailed study of the physical properties of DESs in addition to solving analytical tasks, although we should encourage analysts to pay due attention to the correct use of the terms (D)ES in their publications, as it would certainly help further development in the utilization of DESs in various areas, not just in analytics.

About 20 years ago, Abbott and co-workers researched new solvents that were based on mixtures of choline chloride with urea [1] and carboxylic acids [2] and that were liquid at ambient temperature. The term "deep eutectic solvent" (DES) was later adopted for similar mixtures [1,3]. As DESs have a number of interesting features (the tuneability of their physicochemical properties according to the desired application being just one example), they quickly attracted the attention of researchers and found application in various branches of chemical and materials research. The Scopus database currently returns more than 6,200 hits based on the keyword "deep eutectic solvent" [4].

To date, various definitions of DES have been proposed. Nevertheless, there are still differing views among researchers on what a DES really is and what exact properties a mixture must have in order to be included into this group. Generally speaking, a deep eutectic solvent is a mixture of two or more compounds, a combination of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), that has a lower melting point than those of their individual components [5]. In spite of this, several authors have pointed out that the existence of hydrogen bonding and a eutectic point, as well as the melting point decreasing, are not sufficient to designate a mixture as a DES [6]. We do not wish to

engage in this discussion, as it goes beyond our expertise; we would merely like to summarize some previous views on this issue, especially from the perspective of analytical chemistry.

According to [6], a deep eutectic solvent is a mixture of two or more pure compounds for which the eutectic point temperature is below that of an ideal liquid mixture, presenting significant negative deviation from ideality. The prefix "deep" should therefore only be used for deep eutectic solvents with melting points significantly below ideal predictions [7]. Otherwise, the simpler term "eutectic solvent" (ES) should be used [6–8].

It therefore follows that in order to correctly assign a solvent to the DES or ES group, a phase diagram must be available to evaluate the deviation from the ideality, as well as to quantify the DES's liquid window [9,10]. Unfortunately, only a small number of works has been devoted to phase diagrams, in contrast to the many articles on their application. Furthermore, it would be useful to address some other key issues, such as the formation of DESs, the nature of the interactions between their components, etc., which could also be helpful for further progress in the utilization of these new solvents in various fields.

The use of DESs in analytical chemistry began later, from about the

<sup>\*</sup> Corresponding authors at: Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 80-233 Gdańsk, Poland. E-mail addresses: vasil.andruch@upjs.sk (V. Andruch), plotkajustyna@gmail.com (P. Makoś-Chełstowska), juswasyl@pg.edu.pl (J. Płotka-Wasylka).

middle of the last decade

nevertheless, the number of publications devoted to the use of DESs in this area of research is rapidly increasing [11]. The term DES is now commonly used in analytical chemistry, but authors rarely go into a detailed examination of a DES from the viewpoint of whether it actually is a DES or an ES. Instead, they logically focus mainly on the analytical part, that is, on taking advantage of the benefits that the DES provides. Therefore, it may happen that the solvent used is designated as a DES, even if it does not meet all the necessary requirements.

According to the phase diagrams for binary mixtures, the eutectic point occurs mainly at one specific HBA:HBD molar ratio. In most works, only selected HBA:HBD molar ratios, such as 1:1, 1:2, etc., were investigated. For the purposes of analytical chemistry, only mixtures that are liquid at ambient temperature are of interest [12]. Therefore, more than the exact composition of the eutectic mixture, the so-called liquid window (the composition ranges at which they are in the liquid state) is more important [6,7]. This allows for the tunability of their physicochemical properties depending on the specific application.

#### 1. Concluding remarks

At the heart of the opinion is the need to unify the use of the terminology employed in basic and applied DES research. What is our recommendation for analytical chemists? Researchers should review in detail previously published articles on solid-liquid phase diagrams of DESs that they have used, and if there are similar articles, the conclusions from them, such as melting point and especially a decrease in the melting point compared to the ideal solution, should be given. In the other case, it would be more appropriate to use the term ES instead of DES.

We must also think about the consequences of a similar approach, especially that such a change would complicate literature searches in databases, as researchers who are accustomed to the term DES would continue to search based on this keyword and not find new, relevant articles in which the more correct but lesser-known term ES is used instead of DES. This is why it may be useful to include the word "deep" at least in the keywords.

Of course, we cannot or should not expect analytical chemists to do a detailed study of the physical properties of DESs in addition to solving analytical tasks, although we should encourage analysts to pay due attention to the correct use of the terms (D)ES in their publications, as it would certainly help further development in the utilization of DESs in various areas, not just in analytics.

We would like to know the opinion of analytical chemists on this issue, and we welcome them to join this discussion.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgements

V.A. would like to express his thanks to the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic (VEGA 1/0220/21). J.P.W would like to thank to the National Science Centre of Poland for the financial support given within the grant project (No.: DEC-2020/37/B/ST4/02886). P.M.C would like to thank to the Gdańsk University of Technology for the financial support given within the grant project (No. DEC-12/2021/IDUB/II.AMERICIUM) under the Americium International Career Development - 'Excellence Initiative - Research University'.

#### References

- [1] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, Chem. Commun. (2003) 70-71, doi.org/10.1039/B210714G
- [2] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed, Deep Eutectic Solvents formed between choline chloride and carboxylic acids: Versatile alternatives to ionic liquids, J. Am. Chem. Soc. 126 (2004) 9142-9147, https://doi. org/10.1021/ja048266j.
- [3] E.L. Smith, A.P. Abbott, K.S. Ryder, Deep eutectic solvents (DESs) and their applications, Chem. Rev. 114 (2014) 11060-11082, https://doi.org/10.1021/ cr300162p
- www.scopus.com, Access date: 31.12.2021.
- [5] D.J.G.P. Van Osch, L.F. Zubeir, A. Van Den Bruinhorst, M.A.A. Rocha, M.C. Kroon, Hydrophobic deep eutectic solvents as water-immiscible extractants, Green Chem. 17 (2015) 4518-4521, https://doi.org/10.1039/c5gc01451d.
- M.A.R. Martins, S.P. Pinho, J.A.P. Coutinho, Insights into the nature of eutectic and deep eutectic mixtures, J. Solution Chem. 48 (2019) 962-982, https://doi.org/ 0.1007/s10953-018-0793-1
- L.J.B.M. Kollau, M. Vis, A. Van Den Bruinhorst, A.C.C. Esteves, R. Tuinier, Quantification of the liquid window of deep eutectic solvents, Chem. Commun. 54 (2018) 13351-13354, https://doi.org/10.1039/c8cc05815f.
- L.P. Silva, M.A.R. Martins, D.O. Abranches, S.P. Pinho, J.A.P. Coutinho, Solidliquid phase behavior of eutectic solvents containing sugar alcohols, J. Mol. Liq. 337 (2021) 116392.
- [9] C. Florindo, L.C. Branco, I.M. Marrucho, Quest for green-solvent design: from hydrophilic to hydrophobic (Deep) eutectic solvents, ChemSusChem 12 (2019) 1549-1559, https://doi.org/10.1002/cssc.201900147
- [10] L.J.B.M. Kollau, M. Vis, A. van den Bruinhorst, R. Tuinier, G. de With, Entropy models for the description of the solid-liquid regime of deep eutectic solutions, J. Mol. Liq. 302 (2020) 112155.
- [11] J. Płotka-Wasylka, M. de la Guardia, V. Andruch, M. Vilková, Deep eutectic solvents vs ionic liquids: Similarities and differences, Microchem. J. 159 (2020), 105539, https://doi.org/10.1016/j.microc.2020.105539
- [12] V. Gallo, P. Tomai, M. Gherardi, C. Fanali, L. De Gara, G. D'Orazio, A. Gentili, Dispersive liquid-liquid microextraction using a low transition temperature mixture and liquid chromatography-mass spectrometry analysis of pesticides in urine samples, J. Chromatogr. A 1642 (2021) 462036.

