Measurements of Activity Coefficients at Infinite Dilution of Selected Organic Solutes in a Bio-Based Deep Eutectic Solvent

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Abstract— Upon addressing the environmental challenges in the chemical and petroleum industries, deep eutectic solvents (DES) have been developed as alternatives to traditional solvents. Their advantages over ionic liquids (ILs), including low toxicity, low costs, high biodegradability, easy synthesis, and sustainability, have made them attractive as green solvents. Bio-based DES was used to determine the infinite dilution activity coefficients (IDAC) of n-alkane, alk-1-ene, alcohol, ketone and nitrile by employing gas-liquid chromatography (GLC) technique at temperature ranges of 313.15 to 343.15 K. For the separation of n- n-hexane/hex-1-ene at 313.15 K, selectivity and capacity at infinite dilution were compared with other solvents. The investigated DES indicated poor separation ability compared to those available in the literature and can not be used as a replacement for industrial solvents.

Keywords— Deep eutectic solvents, infinite dilution activity coefficients, gas-liquid chromatography, separation

I. INTRODUCTION

Replacing volatile organic compounds (VOCs) with benign solvents in industrial applications is crucial in developing more sustainable processes. Petrochemical solvents, commonly called traditional solvents, have been widely used in the chemical industry for several years. These solvents are consumed in large quantities due to their availability and low cost. These petrochemical solvents, which are purified via an energy-intensive process, can account for more than 50% of energy costs [1]. These traditional solvents, which generally produce volatile gases, adversely affect the environment by polluting the environment, depleting the ozone layer, posing risks to human health, and are a non-renewable resource [2],[3]. The environmental, sustainability, and health and safety issues relating to these traditional solvents have driven the research on developing alternative environmentally friendly solvent processes/systems to replace traditional volatile organics. Some alternatives to the traditional solvents

that have received extensive attention include ionic liquids (ILs), DESs, and natural DESs.

In recent years, DESs have drawn a magnificent interest in the field of research as alternative solvents for various separation processes [4]. The DES have characteristics identical to the ILs due to their significant properties, such as low vapour pressure and low melting point, and they are non-volatile. Despite being categorised as green solvents, ILs are highly toxic, difficult to synthesise, have high costs, are soluble in water, and have low biodegradability [5]–[7]. The DES has emerged as a solution to overcome the high costs and toxicity confronting ILs.

Activity coefficients at infinite dilution provide incisive information concerning solute–solvent interactions by characterising the intermolecular interaction behaviour of a solute molecule surrounded by the solvent. The activity coefficients at infinite dilution present a better knowledge of the phase equilibrium of high-purity separation processes. Engineers often use this data to synthesise, design, and optimise separation processes of complex mixtures, such as close boiling mixtures and mixtures exhibiting azeotropes or limited miscibility. Activity coefficient provides valuable information for solvent screening purposes for extractive distillation or liquid-liquid extraction and for evaluating alternative processes where it is not feasible to use ordinary distillation.

The gas-liquid chromatography (GLC) method is used to determine the activity coefficients of solutes, whereby the inner part of the chromatic column is coated with the solvent and solutes are introduced with the carrier gas [8]–[10]. The retention times for the solutes in the stationary solvent represent the strength of the interaction of the solute in the solvent. Direct from the experimental values of IDAC, the selectivity and capacity factors can be calculated and it provided critical information on the separation performance of the solvent for separation processes. A high selectivity value will result in the distillation with few equilibrium stages. The capacity is inversely proportion to the amount of solvent used for extraction, hence the lower the capacity the higher the amount of solvent required for extraction.

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II. EXPERIMENTAL SECTION

A. Activity Coefficient Measurements

IDACs were measured using a Shimadzu GC-2014 GC with chromosorb W-HP (80/100 mesh) as a solid support and dry helium as a carrier gas. The packed column was made of stainless steel. It was washed several times using hot soapy, rinsed with cold water and finally flushed with acetone to reduce drying time. A known mass of solvent was coated to a chromosorb (an adsorbent) and was evenly distributed using dichloromethane. While gently shaking the mixture, dichloromethane was constantly evaporated using a vacuum pump. The GC oven temperature was set at $T = 333.15$ K for more than 4 hours until there were no further changes on the column mass. Prior to IDAC measurements, carrier gas was allowed to flow for at least 30 minutes to stabilise the baseline.

The carrier gas flow rate was measured through a calibrated bubble soup flow meter which was placed at the end of the thermal conductivity detector (TCD) vent at 20 mL/min. To calculate the IDAC, the carrier gas flow rate was corrected as to account water vapor pressure in the bubble soap flowmeter. The solute was injected in volumes ranging between (0.2–0.3) μL, which fulfilled the requirements of the sample in the column to be at infinite dilution. Each solute was injected three times for each experimental temperature measurement to check the stability of the experimental conditions. The dead time, t_G, was determined by using air as un-retained pure component for each temperature in the thermal conductivity detector under the assumption that the solubility effects of air in the stationary phase inside the column are insignificant. The temperature used kept solute entering the column in the gaseous state and liquid state over headspace. The outlet pressure was measured using a digital barometer and was the same as atmospheric pressure, as the end of the column is connected to the atmosphere. The deviation of results for the test system reported in Table I was found to be within ±1.76 % and found to agree with the literature [11].

TABLE I
IDAC DATA FOR THE CYCLOHEXANE IN HEXADECANE AT 313.15 K AND P = 101.15 KPA.[A]

Solute	T (K)	IDAC[Exp]	IDAC[Lit]	R.D%
Cyclohexane	313.15	0.794	0.778[11]	1.76

[a] Standard uncertainties u are $u(p) = 1$ kPa and $u(T) = 0.05$ K, of reported values.

III. RESULTS AND DISCUSSION

A. Activity Coefficients at Infinite Dilution Measurements

The five solutes' IDAC values were measured using a packed column. The values were presented in Table II with the temperature ranging from T = (313.15 to 343.15 K) at 10 K intervals.

TABLE II
THE EXPERIMENTAL AVERAGE ACTIVITY COEFFICIENTS MEASURED AT INFINITE DILUTION FOR SELECTED ORGANIC SOLUTES IN THE DES AT T = (313.15, 323.15, 333.15 AND 343.15) K.[A] SOLUTE STANDARD STATES ARE HYPOTHETICAL LIQUIDS AT ZERO PRESSURE.

Solutes	T/K			
	313.15	323.15	333.15	343.15
n-hexane	625.999	583.888	520.687	467.766
hex-1-ene	333.594	315.937	296.761	272.868
methanol	1.623	1.613	1.604	1.594
acetone	7.225	7.194	7.152	7.121
acetonitrile	4.563	4.493	4.420	4.365

[a] Standard uncertainties u are $u(p) = 1$ kPa and $u(T) = 0.05$ K, of reported values.

The deviation of the result for the hexadecane test system was within ±1.76% and agreed with the literature value as shown in Table I. The experimental values of the infinite dilution activity coefficient for five solutes in the DES solvent are presented in Table II at temperatures ranging from 313.15 K to 343.15 K. The packed column coated with the solvent was used in this study and all measured values of IDAC were listed in Table II.

From Table II, the IDAC displayed the following order of sequence: alkane > alkene > ketone >nitrile > alcohol. Futhermore, it was observed that the IDAC values were decreasing with the increase of temperature. This shows the temperature dependence of the IDAC. The IDAC values of all solutes decrease with the increase of alkyl chain length. It was observed that the non-polar solutes consisted of the high values of the activity coefficients as compared to polar solutes. This observed behaviour indicates poor solubility or miscibility of the non-polar solute in the solvent. The low values were observed for all polar solutes. This is attributed to the strong intermolecular forces in the solutes that are acting between polar molecules such as hydrogen bond. As a result, these forces are challenging to break down and are reflected on higher retention times. The high IDAC values signify the poor solubility and miscibility between the solutes and solvent.

The performance of the solvent was assessed using selectivity (S_{ij}^{∞}) and capacity (k_j^{∞}) at infinite dilution as the thermodynamic separation parameters. The industrial separation problem, hexane/hexene, was studied at a temperature of $T = 333.15$ K; the data is reported in Table III. A high-performing solvent should comprise of high selectivity and capacity. Based on Table III results for the separation problem, the studied DES had low capacity compared to other solvents in the literature. For lower values of the capacity, more solvent will be required in separating the selected mixture and it will have a negative impact on the operational costs of the extractive distillation. However, the value of the selectivity was found to be above a unit and comparable with other solvents which is a clear indication that the separation can be achieved for the selected separation problem listed in Table III.

TABLE III
SELECTIVITY AND CAPACITY VALUES OF INVESTIGATED DES IN
THE DES AT 333.15 K.

Solute	$S_{ij}^{\infty} / k_j^{\infty}$
	n-hexane/hex-1-ene
DES	1.88/0.003
[4C1NCl] + [Gly] [1:2][13]	0.78/0.004
[C5C1Pip] [NTf2][12]	1.79/0.185[a]
[C6C1Pip] [NTf2][12]	1.68/0.223[a]
NMP + 3% (w/w) water [14]	1.97/0.102
NFM+ 3% (w/w) water [14]	2.15/0.040

[a] interpolated

IV. CONCLUSION

The experimentally measured IDAC data of five solutes in the DES were presented. Based on the study it was found that the investigated DES showed poor results for the separation problem of n-hexane/hex-1-ene. In this context, DES cannot be used as an alternative to traditional solvents.

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