Glycerol – a Viable Solvent for Absorption of Highly Polar Solutes II: Solubility Temperature Dependence

Jacques J. Scheepers, Edison Muzenda and Mohamed Belaid

***Abstract*—This work is a continuation of our studies on the investigation of the potential of glycerol as a scrubbing solvent for highly polar volatile organic compounds (VOCs) from industrial waste gas streams. The work focuses on the studying the temperature dependence of VOCs solubility in glycerol. Solubility predictions in the form of infinite dilution activity coefficients were performed using the Modified UNIFAC Dortmund group contribution model. It was found that all ethanolamine interactions with glycerol showed a decrease in solubility with increasing temperature and did not necessarily approach ideality. The solubility of organic acids studied increased with increasing temperature, approaching ideality. The solubility of aldehydes decreased with increasing temperature thereby deviating from ideal behavior. However the solubility of the ketone, hydroxy acetone improved with increasing temperature, approaching ideality. The solubility of ethylene glycol was independent of temperature, whilst that of methanol decreased slightly approaching ideality.**

***Index Terms*—Activity coefficients, glycerol, solubility, temperature dependence, UNIFAC.**

I. Introduction

This work is a continuation of our investigation into the viability of glycerol as a suitable scrubbing solvent for the removal of highly polar volatile organic compounds (VOCs) from industrial waste gas streams. In this work the temperature dependence of infinite dilution activity coefficients of selected VOCs in glycerol were computed in order to preliminarily ascertain the ideal operating temperature for absorption operation. Intensive temperature dependence studies have already been conducted on biodiesel ester interactions with nonpolar to moderately polar VOCs [1]–[4]. The results show solubility behaviour variation with VOC family groups.

Preliminary temperature dependence studies on the feasibility of glycerol as a suitable scrubbing solvent was conducted using the Modified UNIFAC Dortmund group contribution model, which was developed in 1987 by Weidlich and Gmehling [5].

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II. Temperature Dependence of Activity Coefficients

VOC removal efficiency from a waste gas stream using an absorption system is influenced by temperature. The temperature dependence of activity coefficients was described by Carlson and Colburn [6] as in (1):

$$\frac{d \ln \gamma_i}{dT} = -\frac{L_i}{RT^2} \quad . \tag{1}$$

In (1), (L_i) is the relative partial molal enthalpy of component (i) referenced to the pure liquid enthalpy at the same temperature (T), with units (cal./ mole), and (R) is the universal gas constant. (L_i) is practically described as the amount of heat absorbed upon the addition of one mole of component (i) to an infinite quantity of solution [6].

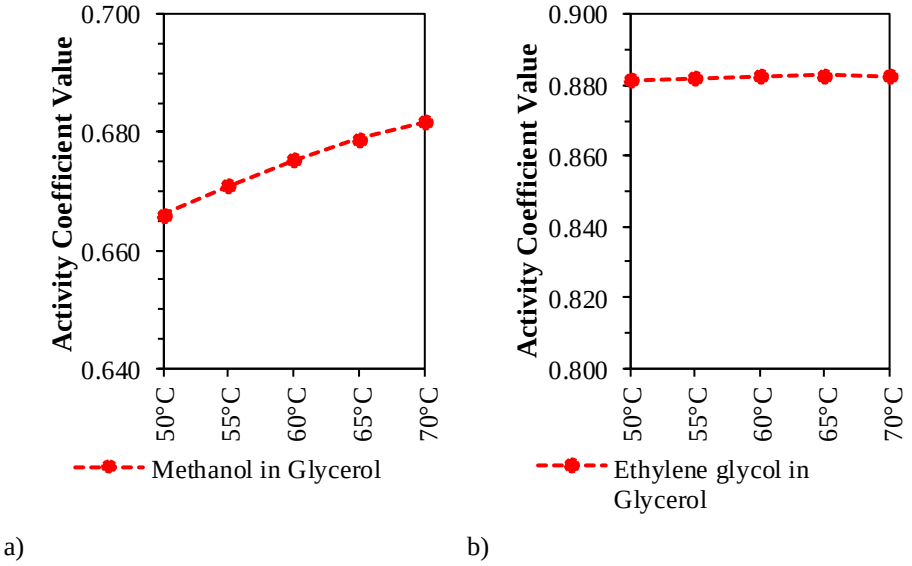
Carlson and Colburn hypothesised that systems of organic component mixtures which deviate positively from Raoult's Law have positive values for molal enthalpy (L), whilst those which deviate negatively from Raoult's Law possess negative values for (L) [6]. This led to the conclusion that organic liquid systems, possessing either positive or negative deviations from Raoult's Law, would thus approach Raoult's Law as a limit with increasing temperature. This would result in activity coefficients ($\gamma_i > 1$) decreasing with an increase in temperature whilst activity coefficients ($\gamma_i < 1$) would increase with increasing temperature. Schiller and Gmehling [7] supported the hypothesis of Carlson and Colburn by stating that for almost all substances, activity coefficients approach ideality (i.e. a value of 1) with increasing temperature. Lower activity coefficients translate to increased solubility which favours the absorption process, but hinders solvent regeneration.

III. Results and Discussion

Infinite dilution activity coefficients were predicted for 12 highly polar VOCs (belonging to five VOC families) in glycerol at various temperatures. Whilst the temperature range of interest for most absorber operations lies between 30° - 40°C [8], a higher temperature range of 50°C – 70°C was selected due to the viscous nature of glycerol at temperatures below 60°C [9] which could hinder mass transfer operations. Computations at temperature increments of 5°C were selected for the purpose of establishing academic trends. A mole fraction of 1×10^{-5} was selected to represent infinite dilution conditions, as recommended by Alessi *et al* [10].

A. Alcohols

The temperature dependence of methanol and ethylene glycol solubility in glycerol is shown in Fig.1.



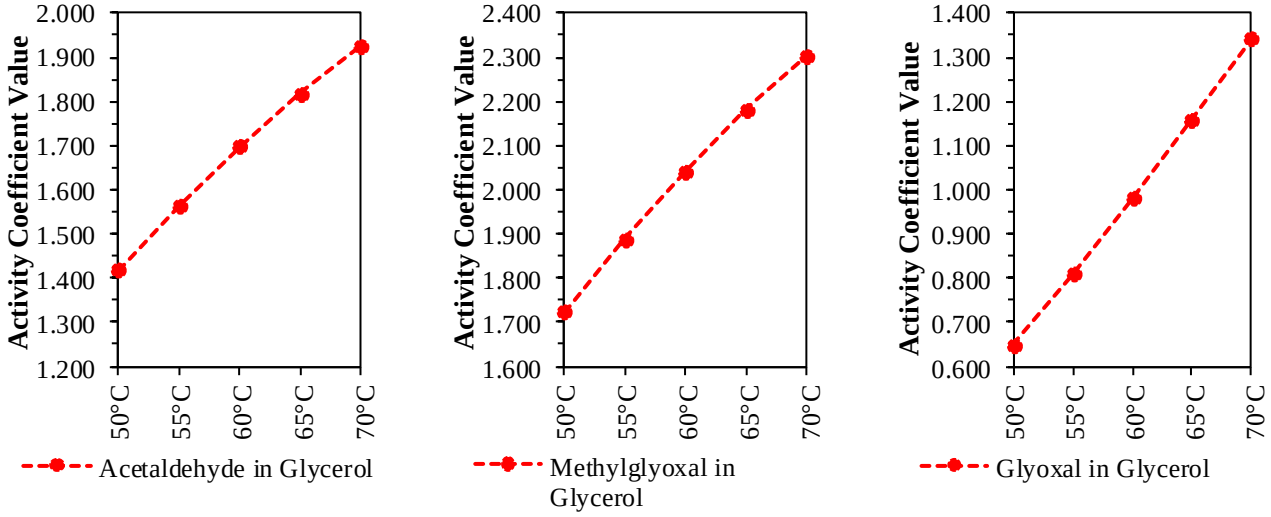
a) b)

Fig.1 Temperature dependence of alcohols in glycerol, (a) methanol; (b) ethylene glycol

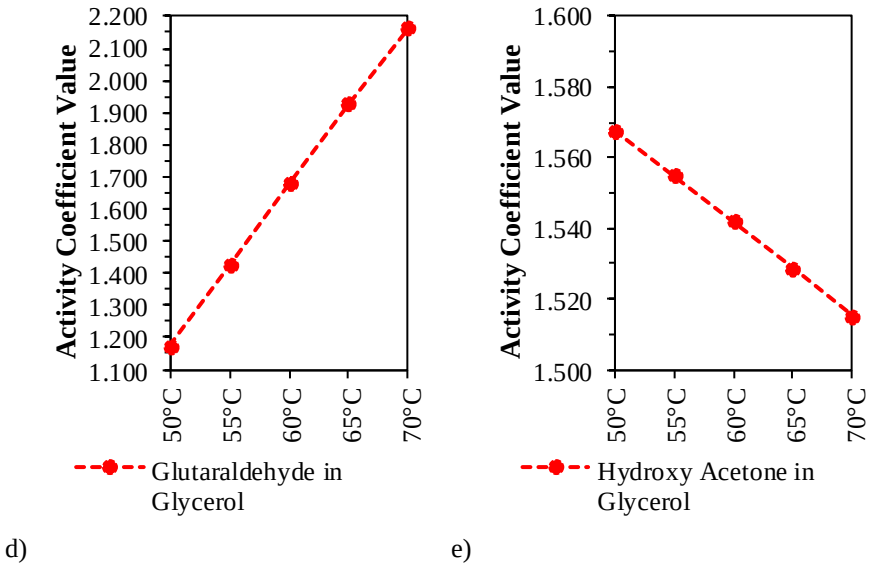
Methanol interaction with glycerol showed a slight increase in activity coefficients (i.e. a decrease in solubility) with increasing temperature, approaching ideal behavior. Ethylene glycol - Glycerol interactions were not influenced by temperature variation. The increase in activity coefficients for methanol- glycerol interactions is possibly due to the increase in kinetic energy imparted to the system with increasing temperature. The increased movement of the molecules does not allow enough time for the solute molecules to come into contact with the solvent molecules for solute-solvent interaction to occur.

B. Aldehydes and Ketones

The temperature dependence of aldehyde and ketone methoxy acetone solubility in glycerol is shown in Fig.2.



a) b) c)



d) e)

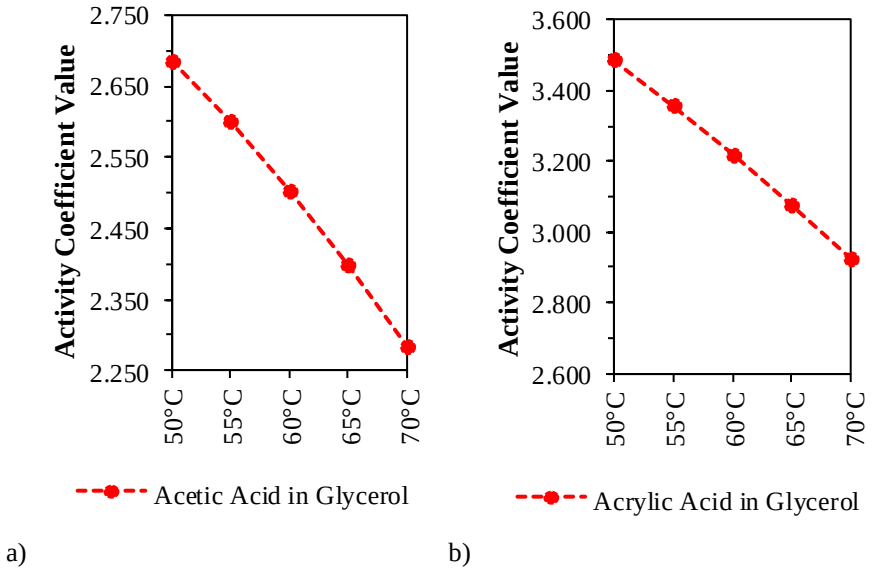
Fig. 2 Temperature dependence of aldehydes and ketones in glycerol, (a) Acetaldehyde; (b) methylglyoxal; (c) glyoxal; (d) glutaraldehyde; (e) hydroxy acetone

The aldehydes showed a decrease in solubility with increasing temperature regardless of whether the activity coefficients were above or below 1. As for methanol, it appears that the increase in molecular movement with increasing temperature inhibited effective contact between the solute and solvent molecules in order to allow for the breaking of solute-solute and solvent-solvent bonds for solute-solvent intermolecular bonding to occur.

Unlike the aldehydes, the activity coefficients of hydroxy acetone decreased with increasing temperature approaching ideality. Since hydroxy acetone has two hydrogen bonding sites (an H-bond donor and an H-bond acceptor site), it seems that the increased energy input into the system assists in overcoming the strong intermolecular solute-solute Keesom interactions in order for solute-solvent bonding to occur.

C. Organic Acids

The temperature dependence of organic acid solubility in glycerol is shown in Fig.3. As for methoxy acetone, organic acids have an H-bond donor and an H-bond acceptor site and thus Keesom solute-solute interactions are also very strong. Organic acids also showed an increase in solubility with increasing temperature, approaching ideal behaviour. As for methoxy ketone, the increased energy input into the system with increasing temperature could serve to break the solute-solute bonds in order to facilitate intermolecular bonding between the solute and solvent molecules.



a) b)

Fig. 3 Temperature dependence of organic acids in glycerol, (a) acetic acid; (b) acrylic acid

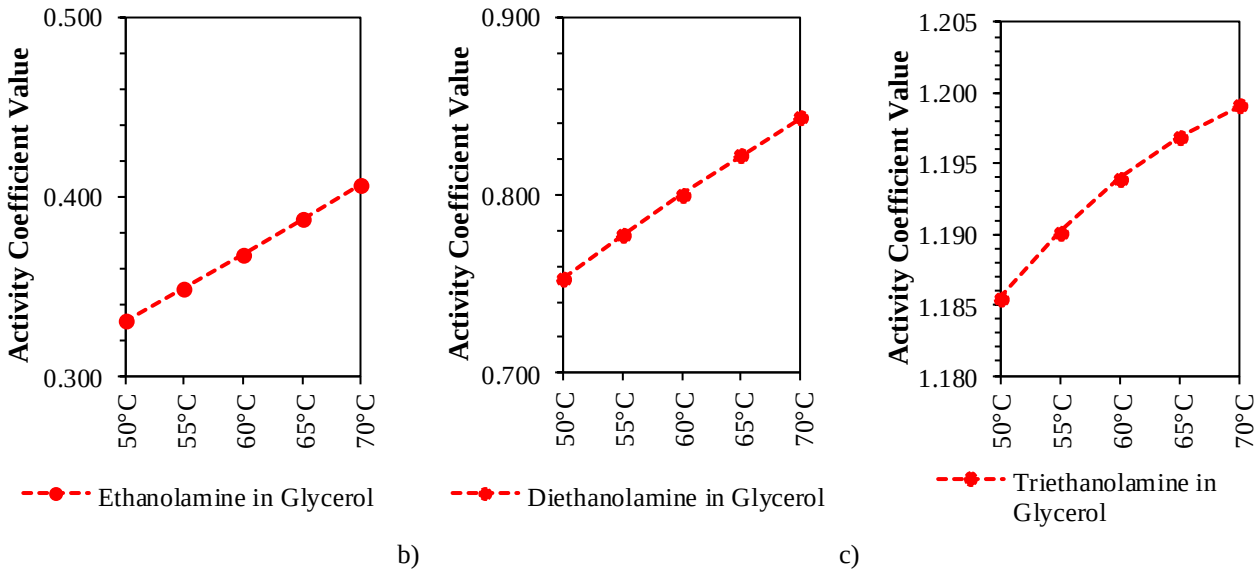


Fig.4 Temperature dependence of ethanolamines in glycerol, (a) ethanolamine; (b) diethanolamine; (c) triethanolamine

D. Ethanolamines

The solubility of all ethanolamines studied decreased with increasing temperature as shown in Fig.4. This resulted in the activity coefficients of glycerol interactions with primary and secondary amines (namely ethanolamine and diethanolamine) approaching ideality whilst those with the tertiary amine triethanolamine deviated from ideality. Thus amines do not necessarily approach ideality with increasing temperature. It appears as if the ethanol chains attached to the amine group of the ethanolamine molecules, being bulky, need more time to align themselves for solute-solvent bonding than is the case for the other highly polar VOCs which have shorter chains. This is increasingly hindered with an increase in temperature, explaining the decreased solubility witnessed in Fig.4.

IV. Conclusion and Recommendations

From the results obtained it is evident that, with the exception of the organic acids and hydroxy acetone, solubility of the VOC families studied decreases with increasing temperature. It is therefore clear that absorption systems incorporating glycerol as a solvent generally favour lower temperature operation with the exception of organic acids and methoxy acetone. Even though it is possible that the results obtained in this work could be inaccurate as diols [11], [12] have to be treated as special groups in UNIFAC modeling this work may be useful for preliminary design calculations. It is recommended that experimental work on the interactions modeled in this work be carried out to evaluate the accuracy of the predictions.

Acknowledgment

The authors are very grateful to the University of Johannesburg's Research Committee and First National Battery, SA for their continued multi-faceted support.

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