

# Temperature Dependence of Limiting Activity Coefficients in C18 Ester Solvents - Part 2

Jacques J. Scheepers, and Edison Muzenda

**Abstract**—This work continued our focus on the influence of temperature on the activity coefficients of biodiesel ester/ VOC (volatile organic compound) interactions. The VOC families studied in this work were alkenes, alkynes, halogenated alkanes and amines. Solubility predictions in the form of infinite dilution activity coefficients were made using the Modified UNIFAC Dortmund group contribution model, and were computed using a Microsoft Excel spreadsheet specifically designed for this purpose. It was found that, with the exception of cyclopentadiene, alkene activity coefficients decreased slightly with increasing temperature thereby generally deviating from ideality. Solubility of alkyne interactions with unsaturated esters increased with increasing temperature, but decreased with saturated ester interactions for the terminal alkynes. With the exception of trichloromethane halogenated alkane activity coefficients decreased with increasing temperature, thus deviating from ideality. Interactions of esters with amines yielded a decrease in activity coefficients with increasing temperature, hence also deviating from ideality.

**Keywords**—Activity coefficients, increasing temperature, biodiesel esters, solubility, van der Waals, UNIFAC.

## I. INTRODUCTION

OUR previous work has already described the influence of intermolecular interactions [1], [2], [7] and the influence of temperature [1] – [6] on ester/ VOC (volatile organic compound) interactions. It was shown that the optimum absorption temperature differs for each VOC family [1], [2], [7]. This work is a continuation of our investigation into the influence of temperature on the activity coefficients of biodiesel ester/ VOC interactions for various VOC families.

The Modified UNIFAC Dortmund group contribution model, developed by Weidlich and Gmehling [8] in 1987 was selected to compute the required phase equilibrium. The phase equilibrium fundamentals, the modified UNIFAC Dortmund group contribution method, computational methodology as well as solvent and thermodynamic model selection have been previously described [1] – [8].

J.J. Scheepers is with the Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, Auckland Park, Johannesburg 2028 (e-mail: jacquess@battery.co.za).

E. Muzenda is a Full Professor of Chemical Engineering, Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, Doornfontein, Johannesburg 2028; phone: 0027-11-5596817; fax: 0027-11-5596430; e-mail: [emuzenda@uj.ac.za](mailto:emuzenda@uj.ac.za).

## II. TEMPERATURE DEPENDENCE OF ACTIVITY COEFFICIENTS

The removal efficiency of a given VOC from a waste gas stream using an absorption system is influenced by the temperature at which the absorption system is operated. Carlson and Colburn used the following expression to describe the temperature dependence of activity coefficients [9]:

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

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 [9].

Carlson and Colburn hypothesised 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 ( $L$ ) [9]. This led to the statement 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. This hypothesis was supported by Schiller and Gmehling, who stated that for almost all substances, activity coefficients approach ideality (i.e. a value of 1) with increasing temperature [10]. Lower activity coefficients translate to increased solubility which favours the absorption process, but hinders solvent regeneration.

## III. RESULTS & DISCUSSION

Infinite dilution activity coefficients were predicted for 17 VOCs in the four C18 methyl esters of varying degrees of unsaturation. The 12 VOCs represented four families of VOCs, namely the alkenes, alkynes, halogenated hydrocarbons and nitrogen-based VOCs. A temperature range of 30 – 50°C was selected for the purpose of establishing trends. A mole fraction of  $1 \times 10^{-5}$  was selected to represent infinite dilution conditions, as recommended by Alessi *et al* [11]. The notation described by Van Gerpen *et al* [12] was adopted to describe

the characteristics of the ester solvent chain, with the prefix '1-' being used to identify the solvent as a methyl ester.

#### A. Ester/ Alkene Interactions

Activity coefficients for the C18 ester solvent/ alkene interactions are shown in Fig.1.

As is the general case with non-polar solutes in ester solvents, solubility of alkenes increased with a decrease in the degree of solvent unsaturation. This is attributed to the increase in bending of the solvent molecule with increasing unsaturation which in turn results in weakened London intermolecular forces. Thus interactions of alkenes with methyl stearate, which is unsaturated, yielded the lowest activity coefficients. With the exception of cyclopentadiene and  $\alpha$ -pinene, activity coefficients of ester/ alkene interactions decreased with increasing temperature, thereby deviating from ideality. It was however also observed that with the exception of cyclopentadiene and  $\alpha$ -pinene, activity coefficients of

alkenes were little affected with increasing temperature.

The cause of the decrease in activity coefficients with increasing temperature is possibly due to the increased energy available to break the weak London forces between solute-solute bonds, increasing the ease in which solute-solvent attractions can occur.

Unlike the other alkenes and its straight-chained counterpart 1,4-pentadiene, the activity coefficients of cyclopentadiene increased with an increase in temperature; hence this solute behaved more like an aromatic compound [7]. Activity coefficients of  $\alpha$ -pinene, being a large complex molecule, were higher than for standard alkenes. Activity coefficients decreased rapidly with increasing temperature, thus tending towards ideality. It is not clear whether  $\alpha$ -pinene naturally tended towards ideality or whether the decreasing trend was as that for all standard alkenes with increasing temperature.

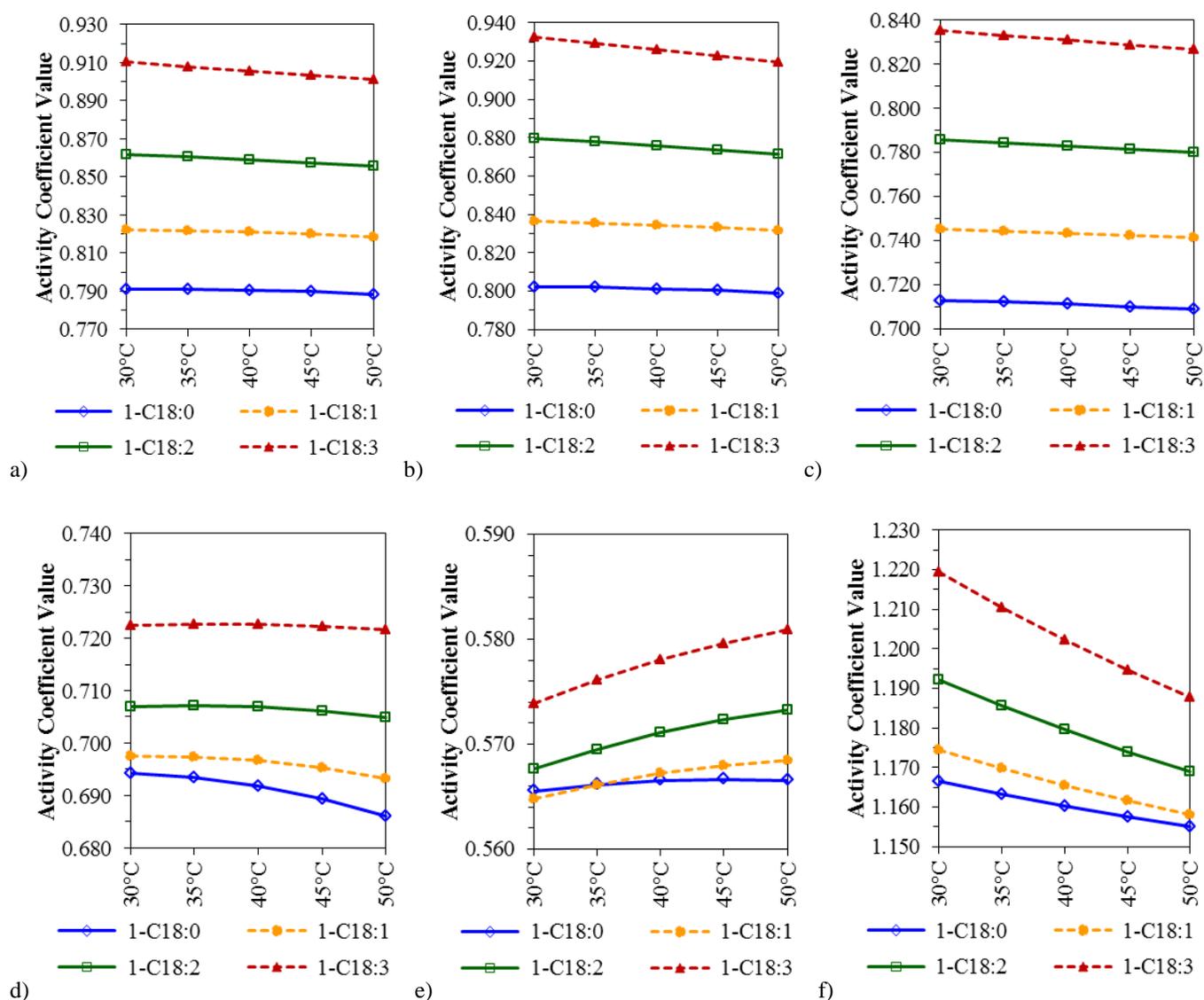


Fig.1 Temperature dependence of alkenes in C18 ester solvents, (a) 1-hexene; (b) 2-hexene; (c) cyclohexene; (d) pentadiene; (e) cyclopentadiene; (f)  $\alpha$ -pinene

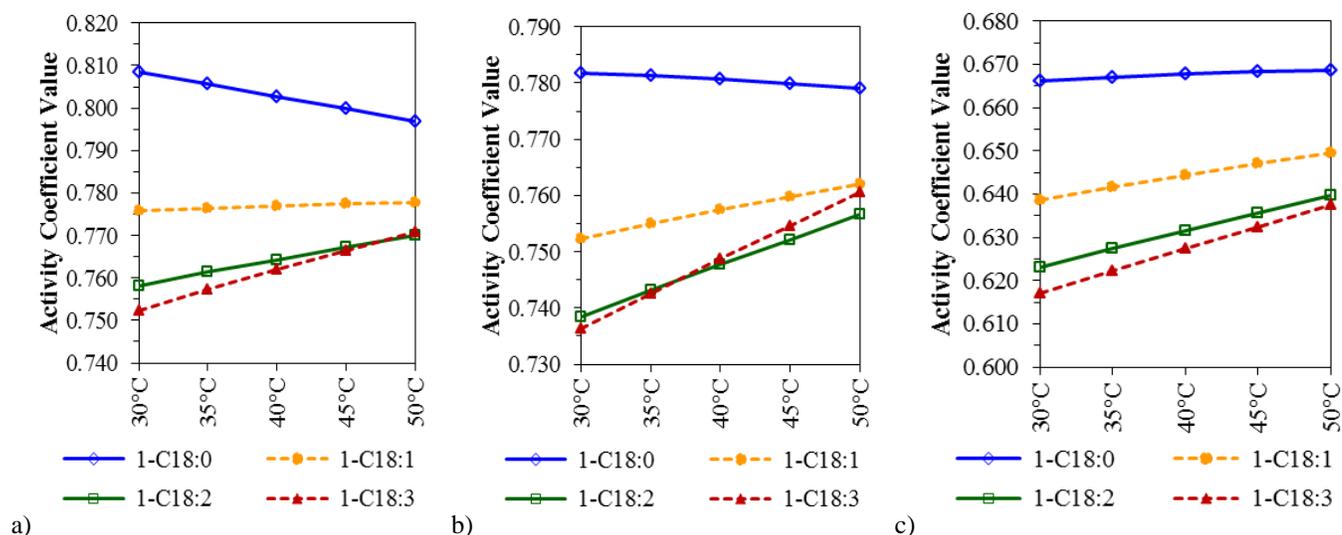


Fig.2 Temperature dependence of alkynes in C18 ester solvents, (a) propyne; (b) 1-butyne; (c) 2-butyne

### B. Ester/ Alkyne Interactions

The interactions between C18 esters and alkynes with increasing temperature are shown in Fig.2.

It was found that, unlike the alkanes [7] and alkenes, alkyne solubility increases with an increase in ester unsaturation especially at lower temperatures. This is attributed to the strong polarising effect of the alkyne triple bond on the ester double bonds. The more double bonds in the ester solvent, the easier the alkyne is attracted to the solvent.

As the temperature increased it was found that the polarizing effect of the alkyne on the solvent decreased. This is possibly due to the increased kinetic energy imparted to the system which did not allow enough contact time between the alkyne and the ester to allow for polarization to take effect. This was possibly the reason for the increase in activity coefficients with increasing temperature. This effect was especially observed for 1-C18:3 ester/ alkyne interactions, which could account for their relatively steep increase in activity coefficients as observed for the terminal alkynes.

It was also observed that unsaturated ester/ alkyne interactions tended towards ideality. This was not the case for the terminal alkynes with methyl stearate. The deviation from ideality observed for saturated ester/ terminal alkyne interactions indicated that the absence of solvent double bonds resulted in these interactions behaving similarly to ester/ alkane interactions.

### C. Ester/ Halogenated Alkane Interactions

The activity coefficients of halogenated alkanes in C18 ester solvents are shown in Fig.3. It was found that, with the exception of trichloromethane, activity coefficients of halogenated alkanes decreased with an increase in temperature regardless of whether the activity coefficients were above or

below that of an ideal solution (an activity coefficient of 1). As for the alkanes [7], the decrease in activity coefficients with increasing temperature was possibly the result of increased energy available to break the weak London forces between solute-solute bonds, which would enhance solute-solvent interactions.

It was observed that the activity coefficients of trichloromethane in ester solvents increased with increasing temperature, thus tending towards ideality with an increase in temperature. The increasing trend was possibly due to the decrease in the strength of Debye and London forces as the kinetic energy in the system increased. This would favour an increase in Keesom interactions between the solute molecules which would reduce the ability of trichloromethane to interact with the solvent.

Brominated alkanes tended to possess higher activity coefficients than the chlorinated alkanes. This was due to the fact that the larger size of the bromine atoms resulted in an increased molecular surface area. Hence brominated alkanes possessed stronger solute-solute London forces, which require more energy to break in order to form solute-solvent interactions than was the case with the chlorinated alkanes.

As for the alkanes [7], brominated alkanes and ethylchloride activity coefficients increased with an increase in solvent unsaturation since the overall electronegativity of these molecules were not high. However an opposite trend was observed for the strongly electronegative dichloroethane and trichloromethane, where solubility generally increased with an increase in solvent unsaturation, due to the high electronegativity polarizing the solvent double bonds.

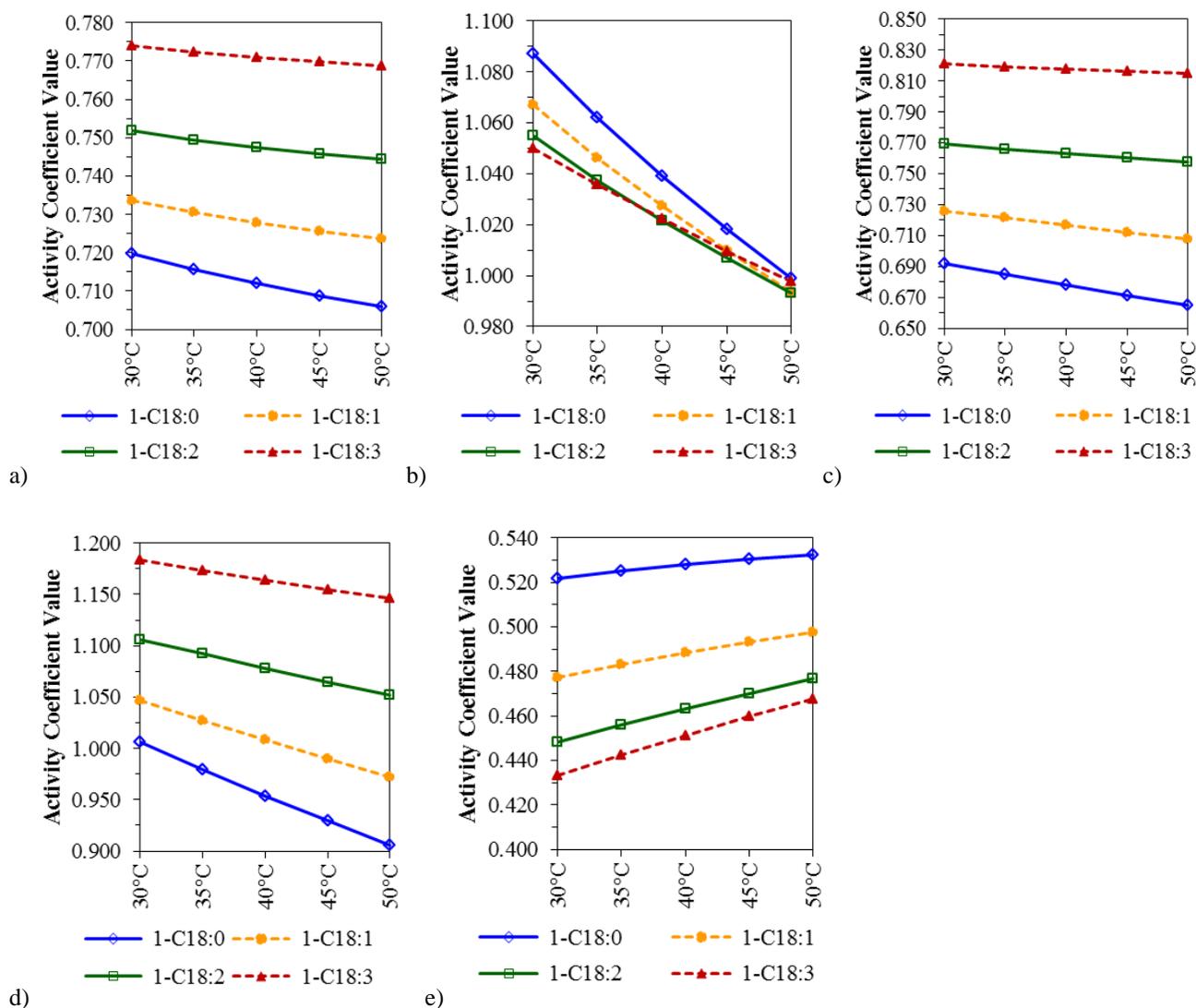


Fig.3 Temperature dependence of halogenated alkanes in C18 ester solvents, (a) ethylchloride; (b) dichloroethane; (c) ethylbromide; (d) dibromoethane; (e) trichloromethane

#### D. Ester/ Amine Interactions

Fig.4 shows the interactions of amines in C18 ester solvents with increasing temperature.

It was observed that the activity coefficients of primary, secondary and tertiary amines decreased with increasing temperature, thereby deviating from ideality. The decreasing trends were attributed to the increase in kinetic energy in the system which assisted in breaking the solute-solute hydrogen bonds to allow for solute-solvent bonding to take place.

It was also found that ester interactions with the primary (ethylamine) and secondary (dimethylamine) amines resulted in a decrease in solubility with increasing solvent unsaturation, whilst the opposite trend was noticed for trimethylamine (a tertiary amine). This is due to the fact that the primary and secondary amines are both H-bond donors, whilst tertiary amines are only H-bond acceptors. This is possibly due to the higher polarity of the primary and secondary amines polarising

the double bonds of the ester solvents. Furthermore the reduced polarity of the tertiary amines would result in non-polar behaviour similar to that of tertiary alcohols [7] due to the shielding of the nitrogen atom.

The activity coefficients of ester/ ethylamine interactions were unexpectedly found to be lower than those of ester/ dimethylamine interactions. The ability of ethylamine to double hydrogen bond should have resulted in higher activity coefficients than those experienced for dimethylamine. It is possible that the length of the non-polar alkyl chain of ethylamine would hinder the effect of the amine's polarity to a certain extent. Furthermore, dimethylamine would be bulky which would hinder London interactions.

It was found that the activity coefficient values of ester/ amine interactions were much lower than that of ester/ alcohol interactions [7]. This is because the amine (NH) hydrogen bond is much weaker than the hydroxyl (OH) hydrogen bond because the oxygen atom is more electronegative than the

nitrogen atom, which results in the hydrogen atom being attracted more closely to the oxygen atom which leaves the hydrogen nucleus more exposed.

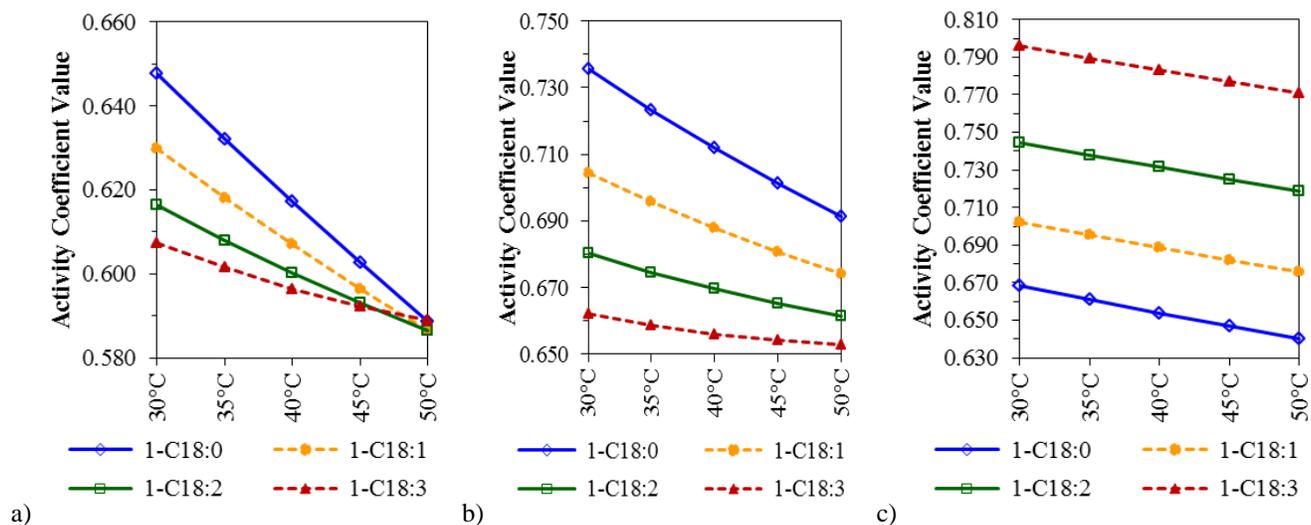


Fig.4 Temperature dependence of nitrogen-based VOCs in C18 ester solvents, (a) ethylamine; (b) dimethylamine; (c) trimethylamine

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