

Interactions of Polar and Nonpolar Volatile Organic Compounds with Methyl Ester Solvents

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Abstract—The interactions of polar and nonpolar volatile organic compounds (VOC) with methyl ester solvents were studied. In order to establish trends two polar and two nonpolar solutes were selected for the study. Solubility computations were performed using the Modified UNIFAC Dortmund group contribution model using a Microsoft Excel spreadsheet. It was found that the solubility of nonpolar solutes in methyl esters increases with an increase in ester chain length, but decreases with an increase in the solute chain length. Furthermore the solubility of nonpolar solutes decreases with an increase in the degree of ester solvent unsaturation. In contrast the solubility of polar solutes in methyl esters decreases with an increase in solvent chain length and increases with increasing solute chain length. Solubility of polar solutes also improved with an increase in the degree of solvent unsaturation. An increase in branching on polar solutes results in an increasing trend towards nonpolar behavior due to the shielding effect of the branches on interactions with the polar site of the solute.

Keywords—Activity coefficients, esters, solubility, van der Waals, UNIFAC.

I. INTRODUCTION

THE imposition of increasingly stringent environmental legislation on chemical industries has resulted in renewed interest in the use of end-of-pipe technologies for removing VOCs from waste gas streams. Since physical absorption processes are proven technologies for treatment of industrial end-of-pipe emissions, the use of ‘green’ solvents as scrubbing agents has been investigated, especially because many of the available scrubbing solvents are themselves also VOCs.

Most VOCs quickly saturate in water, and therefore organic solvents are a good option for the scrubbing of nonpolar and moderately polar solutes from waste gas streams. The use of esters as solvents has recently been investigated. The work of Bay *et al* [1], [2] has shown that biodiesel, a blend of fatty acid esters predominantly in the C16 – C20 hydrocarbon tail range, possesses all the properties of a good solvent for the removal of selected VOCs from waste gas streams, and also because of its biodegradability it is environmentally friendly. [1], [2].

As VOCs are usually present in very dilute concentrations in waste gas streams [3], it is usually impractical and uneconomical to perform phase equilibrium measurements during the preliminary design phase. Prediction of

thermodynamic data such as infinite dilution activity coefficients is thus often necessary using suitable thermodynamic models such as the UNIFAC group contribution method.

This work investigates the differences in interactions between polar and nonpolar solutes in methyl ester solvents through phase equilibrium computations. The Modified UNIFAC Dortmund group contribution model, developed by Weidlich and Gmehling [4] in 1987 was selected to compute the required phase equilibrium data. References [1], [2], [4-11] discussed the modified UNIFAC Dortmund group contribution method, phase equilibrium fundamentals and relevant previous studies.

II. RESULTS & DISCUSSION

Infinite dilution activity coefficients were predicted for 35 VOCs in various methyl esters of varying degrees of unsaturation. Four VOC families were selected, two polar and the other two nonpolar for the purposes of establishing solubility trends. The families selected were the alkanes, alkenes, alcohols and ketones. A mole fraction of 1×10^{-5} was selected to represent infinite dilution conditions, as recommended by Alessi *et al* [3]. 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. Saturated Ester/ Solute Interactions

Interactions between polar solutes and saturated ester solvents are shown in Fig.1. For both alcohols and ketones, activity coefficients decreased with increasing solute chain length, but increased with increasing solvent hydrocarbon tail chain length. Notable exceptions are the lower chain length esters methyl butyrate (1-C4:0) and methyl caproate (1-C6:0) and to a lesser extent methyl octanoate (1-C8:0).

Solubility increased initially for methyl butyrate interactions with both alcohols and ketones, but then decreased. This point was reached at pentanol (5C-OH) and 2-pentanone (2-PENT) for the alcohols and ketones respectively. A slight decrease in solubility with increasing solute size was also found for methyl caproate/ ketone interactions for the higher chain length ketones. This trend was not observed for the alcohols. Alcohols-methyl caproate interactions showed a tapering off of activity coefficients for the higher chain length alcohols. This

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trend was also observed for methyl octanoate interactions with both ketones and alcohols. This is mainly due to the relatively small size of lower of lower chain solvents in relation to the VOC molecules. As the VOCs molecules increase in size the small solvent molecules become increasingly unable to absorb the solute molecules effectively since their intermolecular attractive forces are weaker than the attractive forces between solute molecules. Thus more energy input into the system is required to break the solute-solute interactions.

The reason for the decrease in activity coefficients with polar solute chain length was due to the increased shielding effect of the non-polar hydrocarbon tail with increased solute chain length. Ethanol and acetone, possessing very short hydrocarbon tails, are highly polar, hence the much higher

activity coefficients experienced between these interactions with ester solvents compared to ester/ higher chain length solute interactions. As the solute chain length increases, the non-polar tail portion of the molecule increases in magnitude hindering dipole-dipole (Keesom) interactions. Hence London dispersion forces and dipole-induced dipole (Debye) forces begin to dominate solute-solvent interactions.

The much higher activity coefficients experienced for ester/ alcohol interactions than for ketone/ alcohol interactions can be attributed to hydrogen bonding between solute-solute interactions. These interactions are much stronger than standard Keesom interactions and thus require much more energy input into the system to break these bonds for solute-solvent bonding to occur.

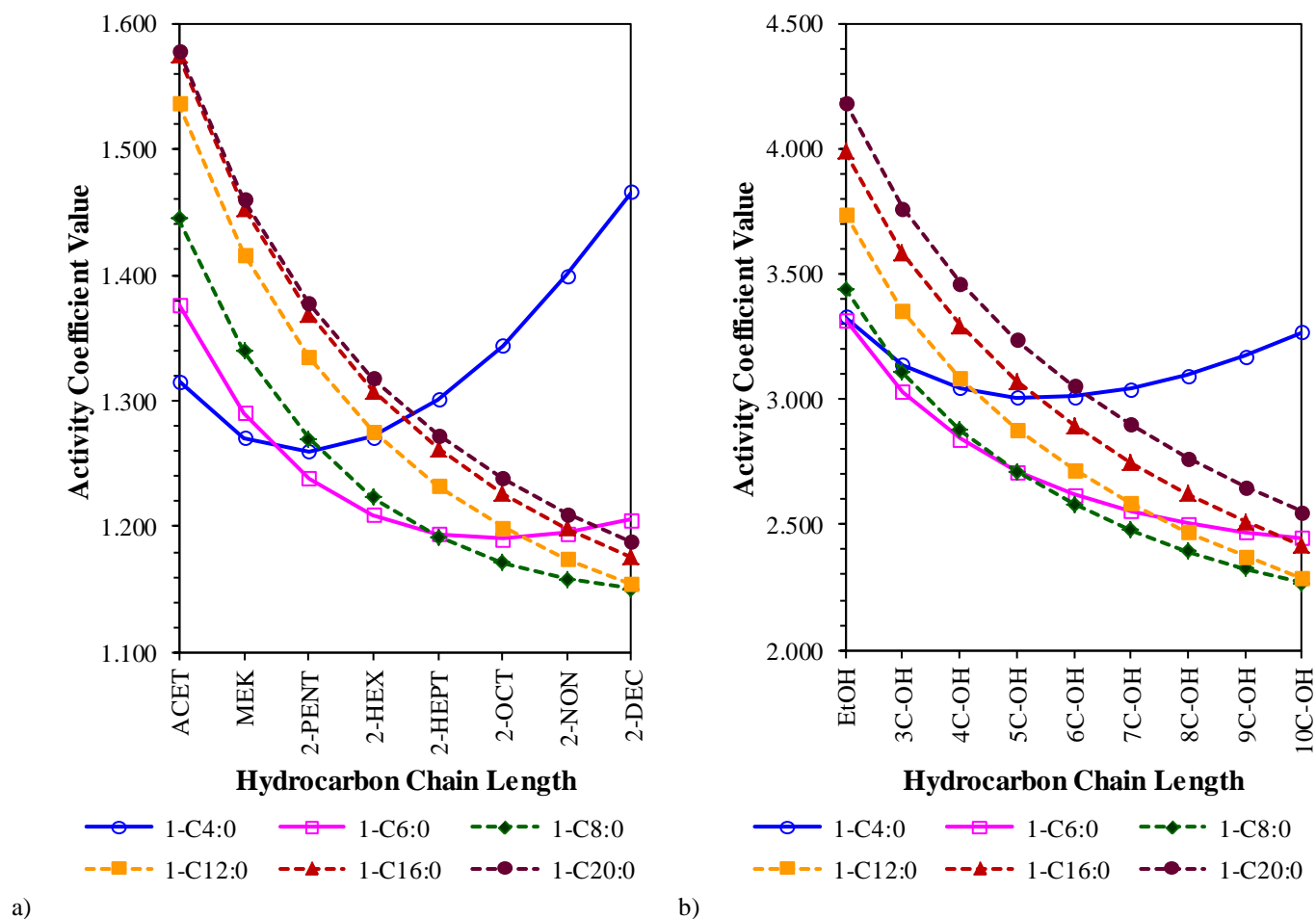


Fig.1 Interactions of polar solutes with saturated ester solvents, (a) ketones; (b) alcohols

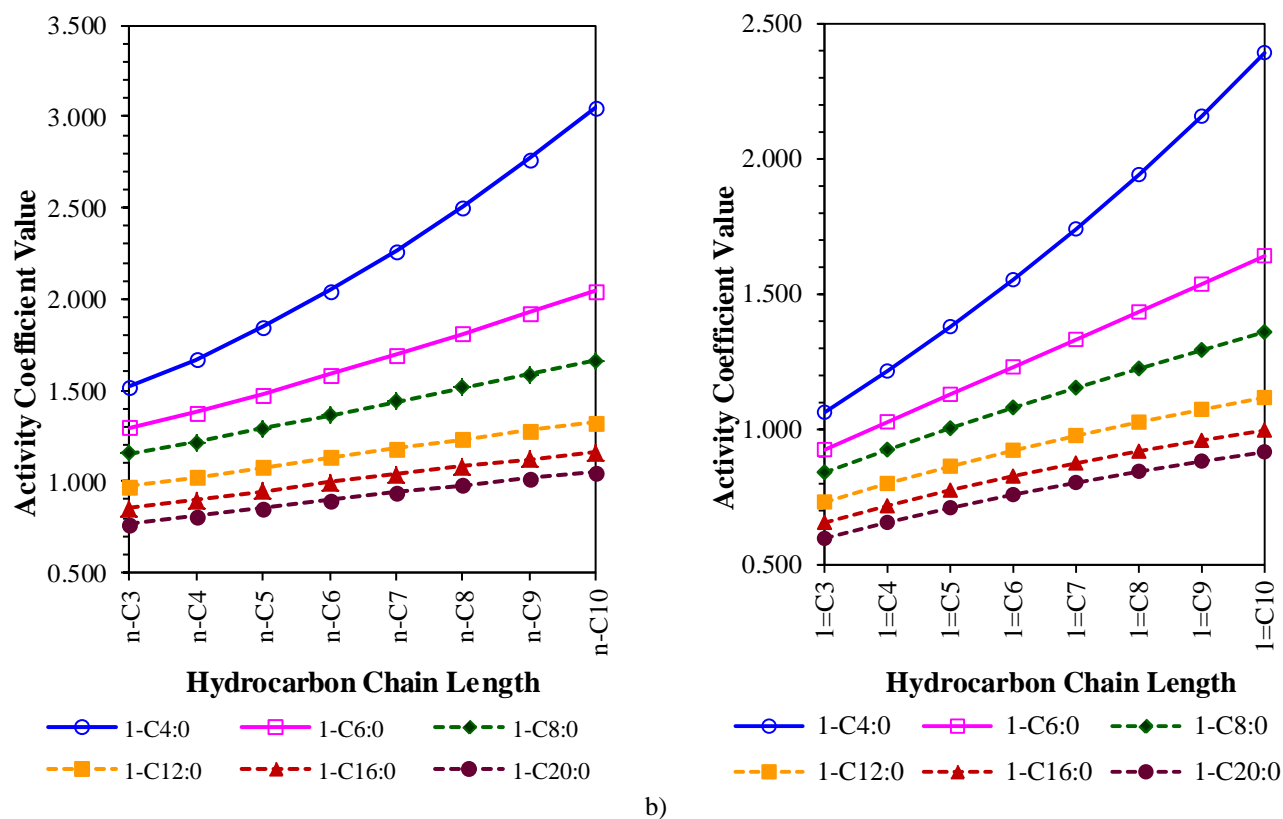


Fig.2 Interactions of nonpolar solutes with saturated ester solvents, (a) alkanes; (b) alkenes

The interactions between nonpolar solutes and saturated esters are shown in Fig.2. Unlike polar interactions with esters, a clear trend of increasing activity coefficients with an increase in solute hydrocarbon chain length was observed. The increase in activity coefficient was more marked with the smaller ester/solute interactions. This is due to the relatively small size of the solvent molecule in relation to the solute molecules whilst the increase is only gradual with the longer-chained esters. The decrease in solubility with increasing solute size was likely due to the increase in the strength of London forces between solute-solute interactions with increased size. Thus more energy would need to be imparted into the system to overcome the solute-solute intermolecular bonds before solute-solvent interaction could occur.

The solubility of alkanes increases with increasing solvent chain length due to the increasing strength of the solvent London forces with increasing solvent size. The stronger the solvent London forces are, the more energy is provided to the system by the solvent to facilitate the breakdown of solute-solute bonds to allow solute-solvent bonding to occur. London forces always dominate nonpolar interactions.

B. Unsaturated Ester/ Solute Interactions

Fig.3 shows the interactions of polar solutes with saturated methyl stearate (1-C18:0) and the unsaturated C18 ester solvents methyl oleate (1-C18:1), methyl linoleate (1-C18:2) and methyl linolenate (1-C18:3).

It was found that activity coefficients decreased with an

increase in the degree of ester hydrocarbon tail unsaturation. The increase in solubility with increased solvent unsaturation was attributed to a polarising effect on the solvent double bonds by the polar head of the solute molecules. An increase in the number of solvent double bonds caused an increase in the polarising effect on the solvent molecule, resulting in increased Debye dipole-induced dipole attractions between the solute and the solvent molecules.

Unlike the C18 ester/ ketone interactions, a converging trend was observed for C18 ester/ higher chain length alcohol interactions. Whereas 1-C18:0 and 1-C18:1 trends decreased uniformly with respect to each other, the higher saturated ester interactions of 1-C18:2 and 1-C18:3 tapered off to converge with 1-C18:0 and 1-C18:1 at higher alcohol solute chain lengths. The tapering of the 1-C18:3 trend was more marked than that of the 1-C18:2 trend. The trends observed for the alcohol interactions with the unsaturated esters were attributed to the effects of hydrogen bonding between the alcohol molecules. It is possible that the increased shielding of the hydrogen bonding site with an increase the alcohol solute size would result in the alcohol solute becoming more nonpolar in nature resulting in London forces beginning to dominate. Since the shape of the solvent molecule becomes more bent with increasing bond unsaturation, less contact surface area is available between the solute and solvent molecules for London forces to work and hence solubility decreases.

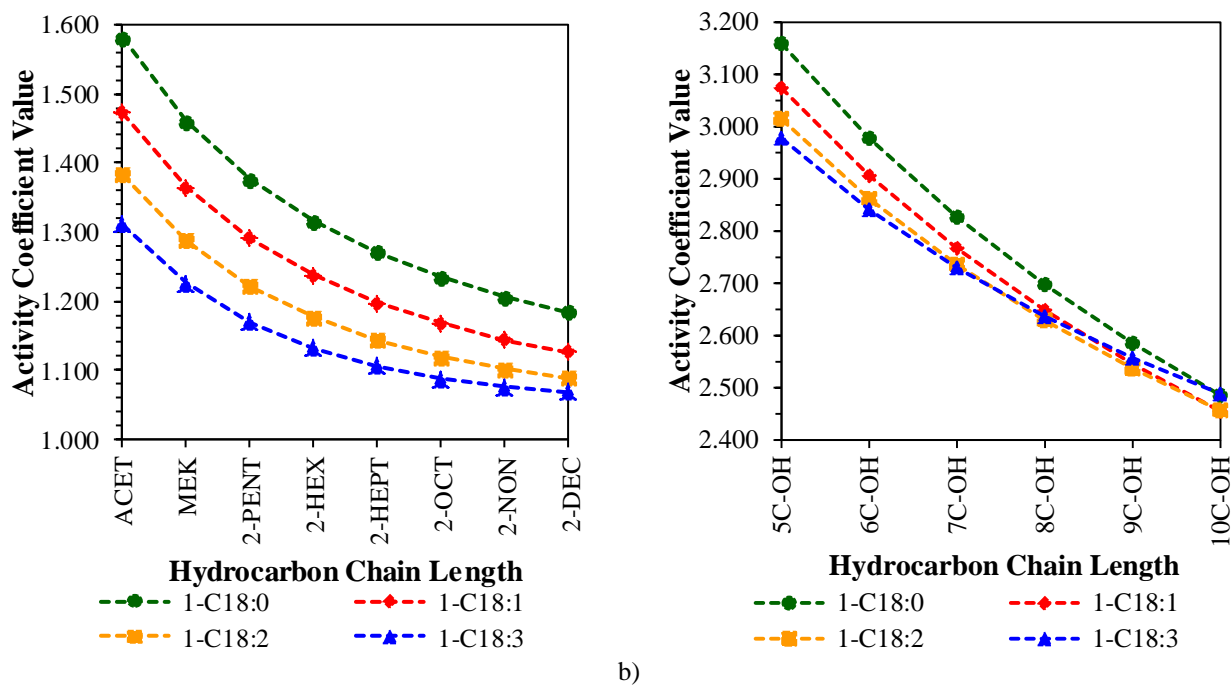


Fig.3 Interactions of polar solutes with C18 saturated and unsaturated ester solvents, (a) ketones; (b) alcohols

In contrast to unsaturated ester/ polar solute interactions, the interactions of nonpolar solutes with unsaturated esters resulted in an increase in activity coefficients with an increase in ester bond unsaturation, as shown in Fig.4. Hence solubility decreased with an increase in the degree of ester unsaturation.

The decrease in absorption capacity with increasing bond unsaturation was attributed to the *cis*-conformation of the

unsaturated double-bonds. *Cis*-conformations result in a 'kinking' of the solvent hydrocarbon tail. An increase in solvent kinking with an increase in the number of double-bonds causes the solvent chain to become increasingly bent. This results in decreasing solvent surface area presented for London interactions between solute and solvent to occur; hence the strength of the solvent London forces decreases.

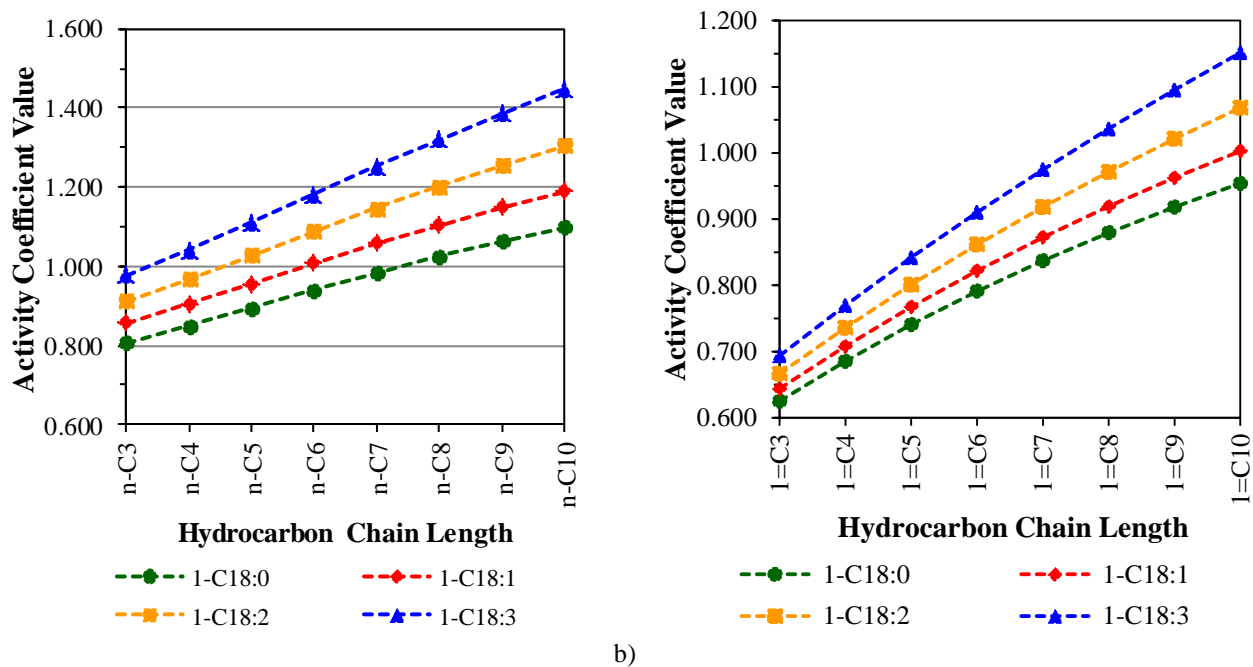


Fig.4 Interactions of nonpolar solutes with C18 saturated and unsaturated ester solvents, (a) alkanes; (b) alkenes

C. Effect of Branching on Ester/ Polar Interactions

The interactions between the different structural isomers of C4 alcohols and C18 saturated and unsaturated esters are shown in Fig.5.

It is evident from Fig. 5(a) that tertiary alcohols yielded lower activity coefficients than primary and secondary alcohols due to the shielding effect of the methyl groups on the polar site making the VOC more nonpolar. Hence solubility

increases with an increase in the degree of branching.

This effect was also experienced with solute interactions with increasing solvent bond unsaturation. The trends began to converge with *sec*-butanol and crossed over with *tert*-butanol due to an increase in the degree of solute non-polarity with an increase in solute branching. The increased shielding resulted in *tert*-butanol being unable to polarise the solvent double-bonds, resulting in nonpolar behaviour.

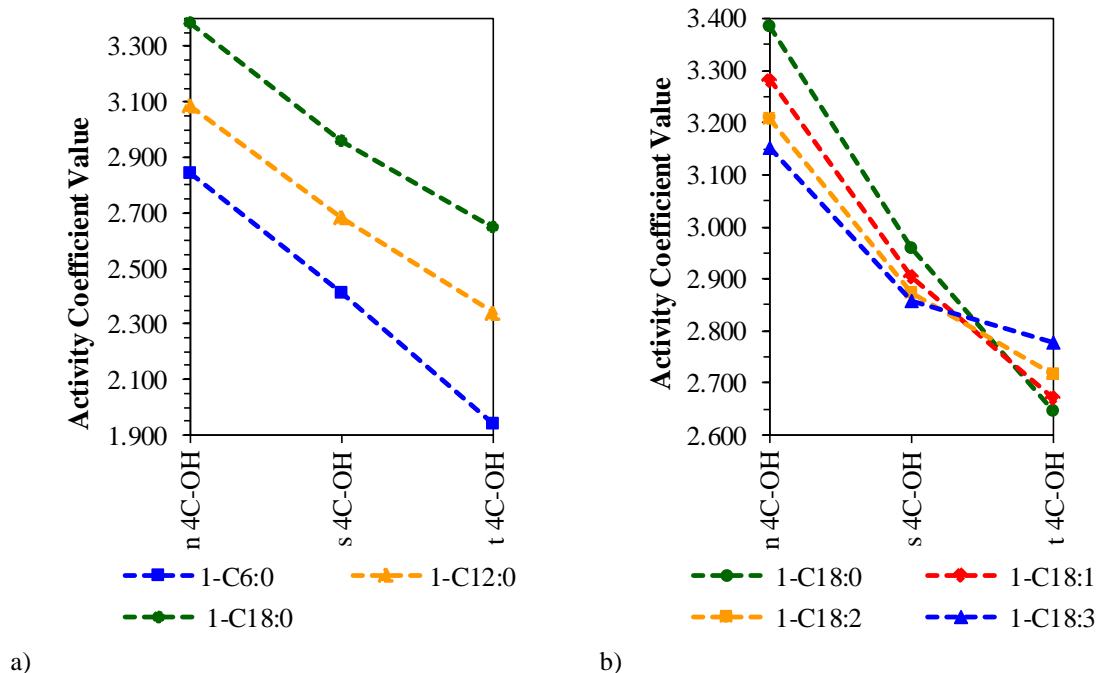


Fig.5 Interactions of structural isomers of C4 alcohol with ester solvents, (a) saturated esters; (b) C18 saturated and unsaturated ester solvents

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