

# MECHANISMS OF FLOCCULATION OF MICROCRYSTALLINE CELLULOSE BY POLY(ETHYLENE OXIDE) AND COFACTOR CORILAGIN

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## 1 ABSTRACT

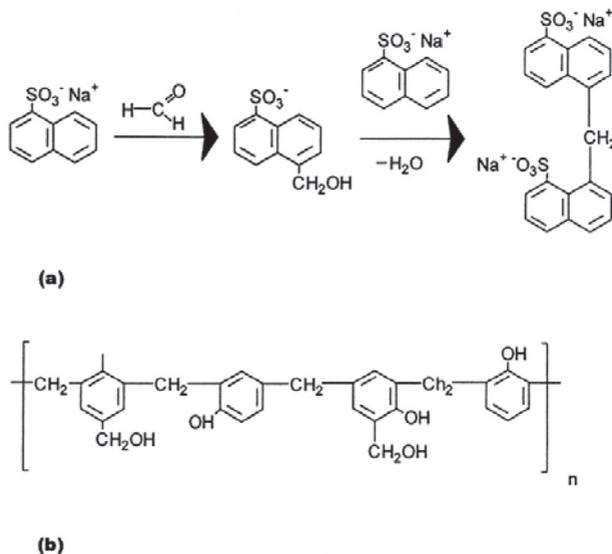
Poly(ethylene oxide) (PEO), a widely known flocculation agent used primarily as a fines retention aid in mechanical grade papers, has its efficiency enhanced by various compounds, known as cofactors. These cofactors form a complex with PEO, which acts as an efficient bridging agent for fines flocculation. The nature of the PEO/cofactor complex is mainly unknown, and it was originally believed that the association was driven by hydrogen bonding. Therefore it was decided to investigate the complex formation in more detail. As a model system we studied PEO and a model cofactor, corilagin, a precursor of tannic acid, a known cofactor for PEO. We performed both Semi-Empirical Molecular Orbital (PM3) gas phase calculations and Molecular Dynamics (MD) calculations in the presence of water. Both methods lead to the

same surprising conclusion: no association between PEO and corilagin occurs at room temperature. The reason is that the gain of association enthalpy is not large enough to overcome the loss in entropy. No correlation was found between the association enthalpy and the number of hydrogen bonds between PEO and corilagin. The absence of PEO/corilagin complexation was confirmed by NMR, isothermal titration calorimetry and the inability of PEO/corilagin to flocculate MCC (microcrystalline cellulose). In the presence of low concentrations of salt, complexation and MCC flocculation was observed.

## 2 INTRODUCTION

Over the last two decades, the paper industry drastically reduced its water consumption which has led to an increase in dissolved and colloidal substances in process waters, which interfere with cationic flocculants. One of the flocculating agents, which is more effective than charged polymers in highly contaminated closed systems, is the PEO(polyethylene oxide)-cofactor retention aid system. The association mechanism between the PEO and cofactor, which is essential to flocculate cellulose fibres, fines and fillers, and aids retention and drainage, is poorly understood. Various cofactors, are believed to associate with PEO, and increase the flocculation efficiency of poly(ethylene oxide) (PEO). Typical industrial examples are phenolic resin and poly(sodium naphthalene sulfonate) (SNS), the structure of which are shown in Figure 1. Originally, this association has been attributed to hydrogen bonding between the ether oxygen in PEO and the cofactor phenolic hydroxyl groups. Recent results have cast doubt on this assumption, as cofactors that could form no hydrogen bonds with PEO (e.g. polynaphthalene sulfonate, polystyrenesulfonate and cofactors with fully dissociated phenolic groups at high pH) were found to be effective cofactors.

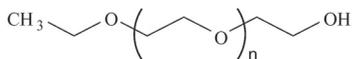
The flocculation of cellulose fibres, fines and fillers, using PEO/cofactor retention aid system, was described by different mechanisms: polymer network formation [2], complex bridging [3], association-induced polymer bridging and asymmetric polymer bridging [4–6], and temperature induced flocculation [7]. Recently, using PEO and tyrosine-containing water soluble polypeptide (TCP), Lu [8] extended the complex bridging [3] mechanism, by considering TCP deactivation and PEO saturation. Association-induced bridging is similar to complex bridging with the difference that it also explains why PEO/cofactor complexes adsorb on pulp fibers.



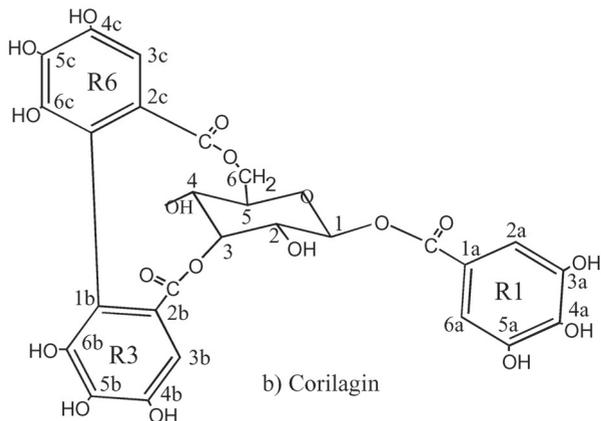
**Figure 1** Molecular structures of a) poly(sodium naphthalene sulfonate) (SNS) (or more precisely the first step in the polymerization of SNS) and b) modified phenolic resin (MPR) [1].

Theoretical Molecular Mechanics [9, 10] calculations, which build in the hydrogen bond, showed that the OH groups of the phenolic rings of the cofactor PFR (Phenol-Formaldehyde Resin) form hydrogen bonds with alternate PEO oxygen 7 Å apart, while the cofactor isotactic PVPh (poly(vinyl phenol)) oligomers, gave hydrogen bonds on every fourth or fifth PEO oxygen and where the  $R-OH \dots O$  distances were  $< 2.37$  Å, with an angle of 130 to 180 degrees. Hydrogen bonding in a water insoluble cofactor PVPh/PEO complex was assumed by Zhang et al. [11], to explain the  $^{13}\text{C}$  solid-state NMR results. The water soluble ionic cofactor PVPh-co-KSS (poly(vinyl phenol-co-potassium styrene sulfonate))/PEO complex, gave  $^1\text{H}$  NMR results that “did not exclude hydrogen bonding” [12], but suggested that other interactions were possible. More recently, Lu et al. [13] found that water soluble polypeptides with high tyrosine contents, phenolic moieties, form complexes with high molecular weight PEO in 1 mM  $\text{CaCl}_2$ .

In this work, microcrystalline cellulose (MCC) particles, which have been used previously in papermaking studies [2, 14–18], were used as a model for fibre fines. Corilagin ( $\beta$ -1-O-Galloyl-3,6-(R)-hexahydroxydiphenoyl-D-



a) PEO



**Figure 2** Molecular structures of a) PEO and b) Corilagin. (R1, R3 and R6 designate rings 1, 3 and 6 respectively) [19].

Glucose) was used as model cofactor [19] (Figure 2). Corilagin has been theoretically [20, 21] and experimentally [22–24] studied. It contains phenolic groups, characteristic of real polymeric phenolic cofactors (see Figures 1 and 2). The bond length, bond angle, heat of formation ( $H_f$ ), Gibbs free energy ( $G$ ), entropy ( $S$ ), and molecular orbital wavefunctions of the complexes PEO/corilagin are discussed.

Experimentally, Isothermal Titration Calorimetry (ITC), Nuclear Magnetic Resonance spectroscopy ( $^1\text{H}$  NMR) and Photometric Dispersion Analysis (PDA) are used to study the interactions in the PEO/corilagin complexes and PEO/corilagin with MCC. Corilagin is studied experimentally, for the first time, as a PEO cofactor for fibre fines flocculation.

### 3 MOLECULAR MODELLING METHODS

The methods to build the conformers have been detailed before [20]. Theoretical calculations followed the procedures previously described [21] using Gaussian GW03 Revision B.02 and GaussViewW Version 3.07 [25–27]. PM3

Semi-Empirical Molecular Orbital Theory was shown to be reliable for conformational analysis of hydrogen bonded molecules [28].

## The complexes

Williams et al. [29] mentioned that, when solvent interactions are ignored, two molecules A and B associate to form a complex, A and B rearrange their structures to give a more stable complex. Recently, Malardier-Jugroot et al. [30, 31], showed that the properties of the solutes and their ability to denature or non-denature proteins can be explained without including the solvent effect.

The PM3 optimised PEO structures capable of forming complexes with the corilagin had intermediate structures,  $A_{opt}$ . The various corilagin (a precursor of tannic acid, a known cofactor) conformers gave  $B_{opt}$ , characteristic of the conformer structure. Equation 1 describes the formation of PEO/corilagin complexes. Initially,  $A_{opt}$  and  $B_{opt}$ , are brought together, changing their conformation to fit into each other,  $A'_{opt}$  and  $B'_{opt}$ , and subsequently re-optimized as a complex to give  $(A' B')_{opt}$ , the most stable possible complex structure.



The PEO hexamer was placed at different positions around the corilagin to give structures interacting at the top, bottom, side and inside the cavity to give the global minimum of PEO/corilagin complexes (Figure 3).

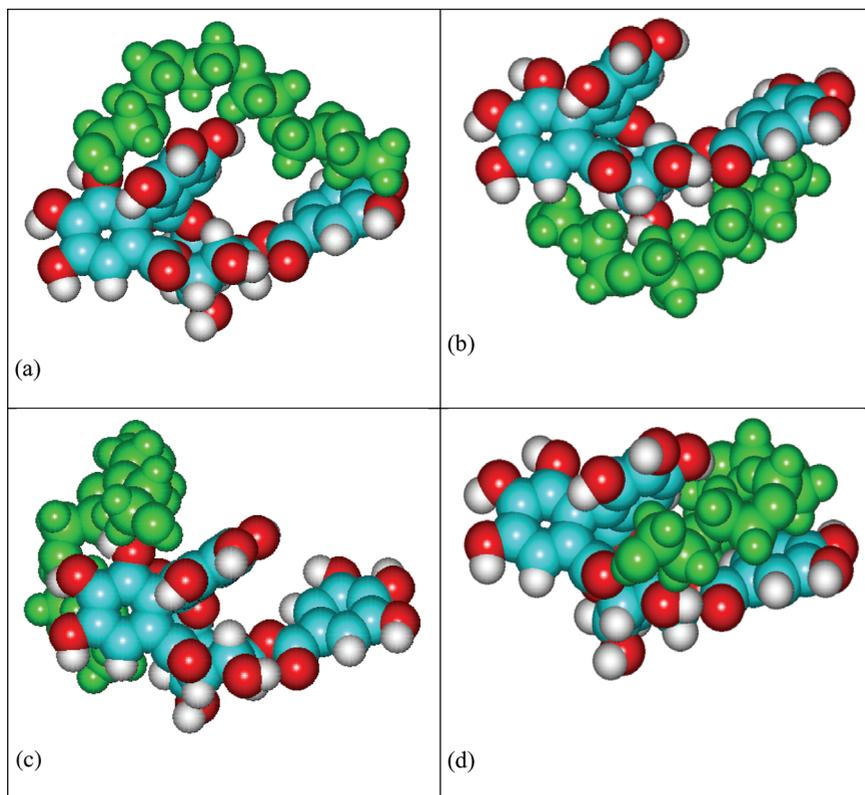
## 4 MATERIALS

### 4.1 Corilagin

Corilagin (1-O-Galloyl-1,3,6-hexahydroxydiphenyl(- $\beta$ -D-glucopyranose), with molecular formula  $C_{27}H_{22}O_{18}$  and molecular weight of 634.08 g mol<sup>-1</sup>, was obtained from Aapin Chemicals Limited (UK). The material, C.A.S. 23094-69-1, is natural in origin, with purity  $\geq 95\%$ . The pH of a 5 ppm corilagin solution is 5.0.

### 4.2 Poly(ethylene oxide)

Laboratory grade PEO with molecular weight of 900 kDa and a polydispersity index of 1.11 was used for the NMR and ITC experiments. For the stability ratio experiments, a commercial hydrophobically modified PEO, MaxiFloc 998 lot # I334, provided by E.Q.U.I.P. International inc, Baie



**Figure 3** Complexes of (PEO)<sub>6</sub>/corilagin-boat with different locations of the PEO hexamer; (a) on top, (b) below, (c) beside and (d) inside the cavity of the cofactor corilagin-boat, are shown.

d'Urfé, QC, Canada, was used. This PEO has an average molecular weight of about 10M; 95% being in the 8–11M range and 5% less than 100,000.

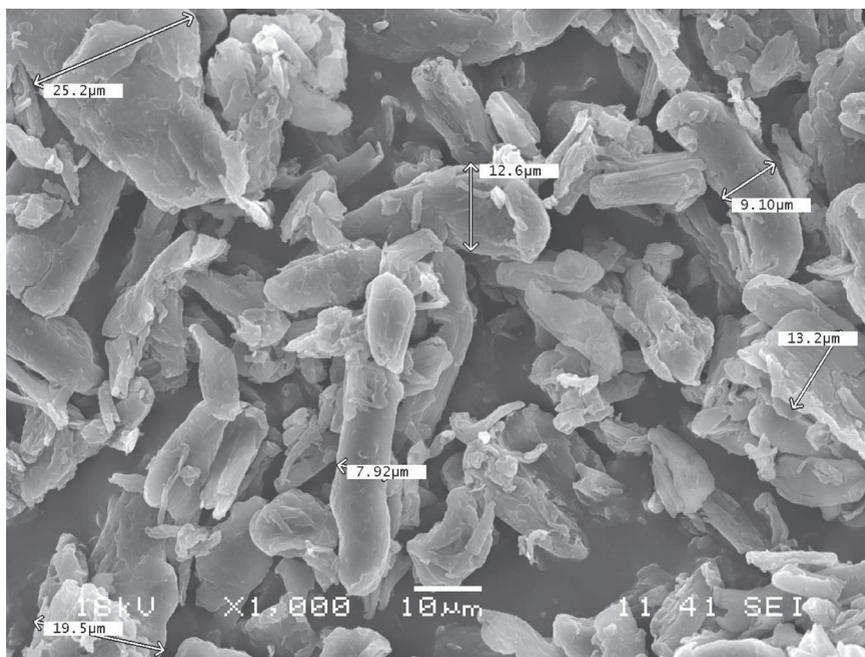
### 4.3 Potassium chloride

The electrolyte (KCl) was reagent A.C.S. grade, +99.0% purity, from APC Produits Chimiques, Montreal, Qc, Canada.

#### 4.4 Microcrystalline cellulose

Avicel PH 105 microcrystalline cellulose (MCC) was supplied by FMC Corporation, Philadelphia, PA., as a white powder. The MCC particle size closely resembles to a log normal distribution with an average of  $24.6 \mu\text{m}$  for the powder, and  $21.6 \mu\text{m}$  for a 1.5% suspension [32]. The pH of the 1.5% suspension was 5.04.

Scanning Electron Microscopy (SEM) showed this material to be irregular in shape and polydisperse (Figure 4). MCC is negatively charged [15], with surface ionic charge of  $-4.6 \text{ meq kg}^{-1}$  (dry basis) at pH 5.04, measured by a streaming potential titrator (Mütek) using polyDADMAC ( $M_w = 107000 \text{ g mol}^{-1}$ ) as the titrant.



**Figure 4** SEM of MCC particles showing that they are irregular in shape and polydisperse.

#### 4.5 De-ionised water

Water from the Nanopure, Ultrapure water system, Barnstead Model No. D4744, was used for the stability ratio experiments. The conductivity of the treated water varied from  $1.17$  to  $6.9 \mu\text{S/cm}$  corrected at  $25^\circ\text{C}$ .

## **5 EXPERIMENTAL METHODS**

### **5.1 Magnetic resonance spectrometer**

All experiments were performed on a Varian Mercury 300 MHz, using D<sub>2</sub>O as solvent. D<sub>2</sub>O was purchased from Cambridge Isotopes Laboratories, Inc. Andover, MA, USA.

### **5.2 Isothermal titration calorimetry**

Thermal titrations were carried out using an ultra-sensitive isothermal titration calorimeter (VP-ITC) from MicroCal, LLC (NorthHampton, MA). Before the titration, all samples were degassed using a MicroCal Thermo-Vac for five minutes. The differential power (baseline) between the sample cell and the reference cell was 5  $\mu\text{Cal}/\text{sec}$ . Titration data were processed by MicroCal Origin version 5.0 and background titration heat was not subtracted. In the isothermal titration calorimetry experiments, about 0.6 g/L PEO was gradually added, drop by drop (10  $\mu\text{L}$  per drop) in either H<sub>2</sub>O or D<sub>2</sub>O at 30°C, to a 0.4 g/L corilagin solution, and the resulting heat effect of each injection was measured. The time interval between drops was 230 seconds and the temperature remained constant. No buffer was used, because corilagin and PEO are neutral. The results are expressed as heat flow into the calorimeter, so a positive heat reading indicates an endothermic reaction, and a negative reading an exothermic reaction.

### **5.3 Particle size analyser**

Particle size analyses were performed using a Malvern Hydro 2000 S (A) instrument. The refractive index of cellulose, which is 1.55, was used for MCC. Results for MCC are an average of five measurements, with a stirring rate of 1925 rpm and no ultrasound.

### **5.4 Flocculation (Photometric Dispersion Analyzer)**

Changes in the state of aggregation of MCC (model fines) were monitored by a Photometric Dispersion Analyzer (PDA 2000 Rank Brothers, Cambridge UK) [17, 33]. Change in the ratio,  $R$ , of the root mean square variations in transmittance relative to the mean transmittance were measured as a function of time. Changes in  $R$  are mainly due to changes in the sizes of the flocs, and the initial slope of  $R(t)$  is approximately proportional to the flocculation rate  $k_f$ . The stability ratio  $W$  for a particular flocculation rate  $k_f$ , is [18]:

$$W = \frac{k_{fast}}{k_i} \cong \frac{(dR/dt)_{fast}}{(dR/dt)_i} \quad (2)$$

where  $k_{fast}$  is the fastest rate of flocculation described by  $\log W = 0$ : when  $\log W = \infty$  the suspension is stable. The total suspension volume was 1 L. The suspension was stirred at 100 rpm using a Teflon blade propeller, 9cm  $\times$  3cm. The concentration of MCC was 300 mg L<sup>-1</sup>, and the pH was 6.6–6.7 before the addition of PEO and cofactors. Flow rates were  $\sim$ 75 to 100 mL/min. Experiments with PEO/corilagin systems were carried out with different concentrations, and corilagin:PEO ratios.

## 6 RESULTS AND DISCUSSION

To analyse the complexation theoretically it is necessary to study first PEO and corilagin in isolation, followed by the interactions among them.

The heat of formation of the hexamer of PEO at 0°K is  $H_{f,0^{\circ}K} = -256.71$  kcal mol<sup>-1</sup>. The hexamer ((PEO)<sub>6</sub>) was used to ensure that the linear length is greater than the model cofactor size to minimize end group effects (CH<sub>3</sub> and OH).

### 6.1 (PEO)<sub>6</sub>/Corilagin

Corilagin has two phenolic rings (R3R6) joined, and has two boat conformers, *boat* and *skew-boat*, with heats of formation of -650.24 and -652.23 kcal mol<sup>-1</sup> respectively [21] (Table 1). These conformers were used to study the interactions with PEO. Table 2 shows that the (PEO)<sub>6</sub>/corilagin skew-boat complex is the most stable with an enthalpy of association at 298.15°K of  $\Delta H_{298^{\circ}K} = -16.78$  kcal mol<sup>-1</sup>. The (PEO)<sub>6</sub>/Corilagin-boat complex shows no dependence of the heat of formation ( $\Delta H_{298^{\circ}K}$ ) on the number of intermolecular H-bonds (Table 2 and Figure 5). For example for a decrease from 4

**Table 1** Heats of formation of the corilagin conformers

| Cofactor   | Conformer | $H_{f,0^{\circ}K}$ (kcal mol <sup>-1</sup> )<br>PM3/GW03 |
|------------|-----------|--|
| Corilagin* | Boat      | -650.24  |
| Corilagin* | Skew-boat | -652.23  |

\* Corilagin has a covalent bond between R3 and R6.

**Table 2** Thermochemistry for the association of PEO hexamer and corilagin conformers at 298.15°K.

| Complexes  | Conformer | $\Delta G_{298^{\circ}K}$<br>(kcal/mol) | $\Delta H_{298^{\circ}K}$<br>(kcal/mol) | $T\Delta S_{298^{\circ}K}$<br>(kcal/mol) | Inter-<br><i>R-OH...O*</i> |
|--|-----------|---|---|--|----------------------------|
| (PEO) <sub>6</sub> /Corilagin                    | Boat      | 14.13                                   | -12.45                                  | -26.58                                   | 4**                        |
| (PEO) <sub>6</sub> /Corilagin                    | Boat      | 10.62                                   | -12.25                                  | -22.87                                   | 1                          |
| (PEO) <sub>6</sub> /Corilagin                    | Skew-boat | 7.73                                    | -16.78                                  | -24.50                                   | 1                          |
| (PEO) <sub>6</sub> /corilagin/(PEO) <sub>6</sub> | Boat      | 23.30                                   | -20.44                                  | -43.74                                   | 4*                         |
| (PEO) <sub>6</sub> /corilagin/(PEO) <sub>6</sub> | Skew-boat | 18.14                                   | -23.32                                  | -41.46                                   | 1                          |

\* Judged by distance only.

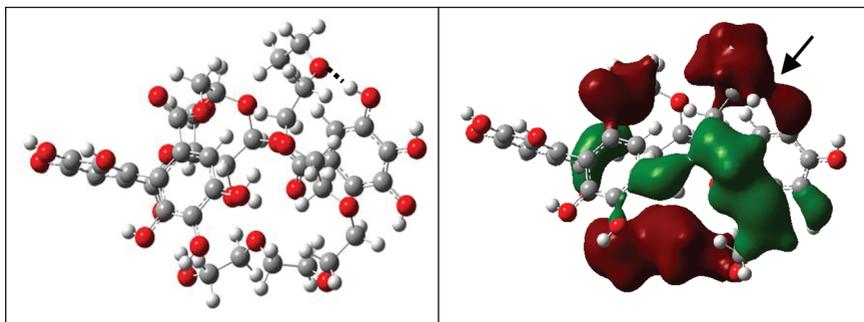
\*\* One bond is of the *R-CH...O* type.

to 1 hydrogen bonds, the enthalpy of association  $\Delta H_{298^{\circ}K}$  are -12.45 and -12.25 kcal mol<sup>-1</sup> respectively (Table 2). Three of these bonds are of the *R-OH...O* type while one bond is of the *R-CH...O* type (Table 2).

The (PEO)<sub>6</sub>/corilagin complexes do not form at room temperature because  $T\Delta S$  is too large, making  $\Delta G > 0$  ( $\Delta G = \Delta H - T\Delta S$ ) (Table 2).

The behaviour of (PEO)<sub>6</sub>/corilagin complexes is different from stable systems studied by Alkorta and Elguero [34] who found that the interaction energy in different complexes follows an exponential relationship with respect to the number of *R-OH...O* bonds.

Figure 5 shows DLMO 9, out of 174 occupied DLMOs, which totally



**Figure 5** Molecular structure of (PEO)<sub>6</sub>/Corilagin-boat complex showing the *R-OH...O* bond (dotted line, left and arrow, right), and the corresponding DLMO 9 with eigenvalue -1.453 eV. Notice the distinct narrowing of the electron density at the centre of the H-bond.

covers one hydroxyl and an ether oxygen of the PEO,  $R - OH \dots O$ , traditionally described as a “hydrogen bond”. Considering DLMO 9, only, a part of the wavefunction is found to cover the  $H \dots O$  atoms. Notice the characteristic “pinch” of the orbital in the  $R - OH \dots O$  region.

Table 3 shows three types of interaction: (i)  $R - OH \dots O$ , (ii)  $R - CH \dots O$ , and (iii)  $R - CH \dots H$ , where  $R - OH \dots O$  is the traditional “hydrogen bond”. The other types have been discussed in the literature [32, 35, 36].

There is a possibility that the cofactor can be complexed from top and bottom, therefore sandwich complexes must be considered.

**Table 3** Bond characterization in  $(PEO)_6$ /Corilagin-boat complex.

| Inter-atomic interactions           | Inter or <i>intra</i><br>H-bond | Bond length<br>(Å) | Bond angle<br>[°] |
|-------------------------------------|---------------------------------|--------------------|-------------------|
| $R_{phenol} - OH \dots O_{ether}$   | Inter                           | 1.818              | 163.84            |
| $R_{phenol} - OH \dots O_{ether}$   | Inter                           | 1.820              | 165.76            |
| $R_{PEO} - OH \dots O_{Carbonyl}$   | Inter                           | 1.846              | 168.74            |
| $R_{Sugar} - OH \dots O_{Carbonyl}$ | <i>Intra</i>                    | 1.812              | 154.66            |
| $R_{PEO} - CH \dots O_{Sugar}$      | Inter                           | 1.872              | 175.44            |
| $R_{PEO} - CH \dots H_{phenol}$     | Inter                           | 1.714              | 150.67            |
| $R_{PEO} - CH \dots H_{phenol}$     | Inter                           | 1.755              | 138.41            |

## 6.2 $(PEO)_6$ /Corilagin/ $(PEO)_6$

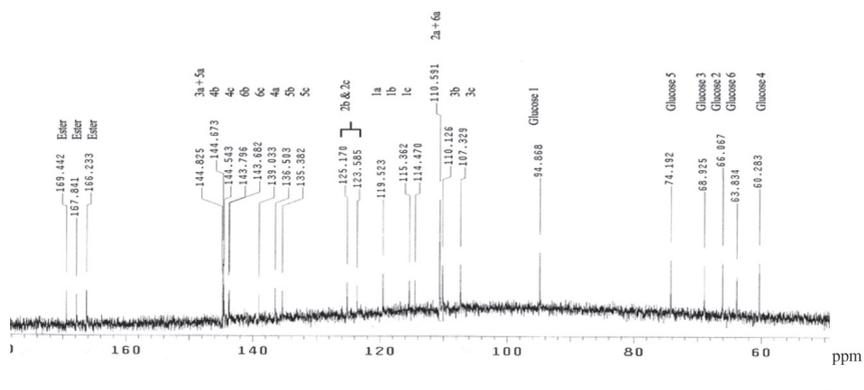
When corilagin conformers associate with one and two PEO hexamers, the enthalpy of association at 298.15°K increases by a factor of 1.64 for the boat, and 1.39 for the skew-boat conformers (Table 2). Again no association occurs at 298.15°K because of high entropy. Again, there is no correlation between the number of inter-molecular “H- bonds”, and the enthalpy of association for the corilagin complexes (Table 2).

## 6.3 Solvated system: $(PEO)_6$ /Cofactor/ $(H_2O)_n$

Semi-Empirical Molecular Orbital calculations and Molecular Dynamics calculations in the presence of water  $(H_2O)_n$  lead to the surprising conclusion that no association between  $(PEO)_6$  and cofactor occurs at room temperature [32].

## 6.4 $^{13}\text{C}$ NMR

The  $^{13}\text{C}$  solution NMR spectrum of corilagin in  $\text{D}_2\text{O}$  shows the signals of 27 carbons (Figures 2 and 6): three ester, six glucose and 18 galloyl carbons, consistent with the molecular formula  $\text{C}_{27}\text{H}_{22}\text{O}_{18}$  and with the results of Jochims et al. [22], and Yoshida and Okuda [23]. This spectrum does not show whether or not the glucopyranoside ring of corilagin has a skew-boat conformation, as found experimentally [23] and theoretically [21].



**Figure 6** Experimental  $^{13}\text{C}$  NMR spectrum of corilagin in  $\text{D}_2\text{O}$  at room temperature. Numbering refers to Figure 2.

## 6.5 Absence PEO/corilagin association in pure water

### 6.5.1 Isothermal titration calorimetry

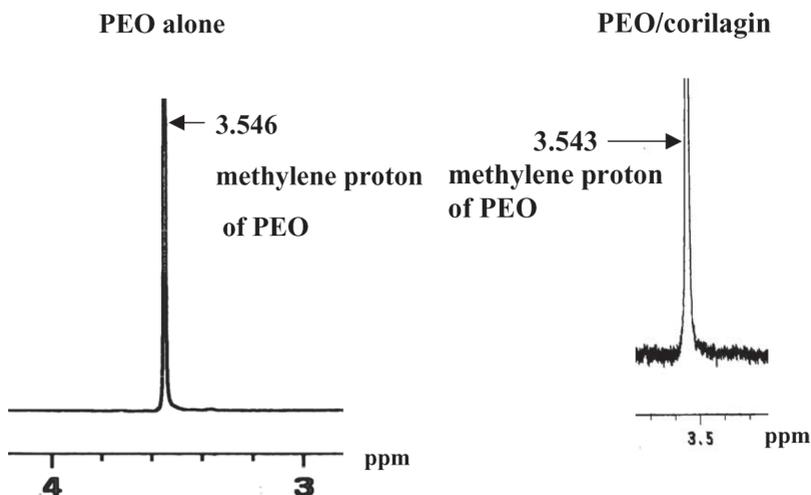
ITC was performed in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  to determine whether the solvent modifies the interactions between PEO and corilagin in pure water. By titration of the corilagin containing the phenolic rings with PEO, the  $\text{CH}_2\text{CH}_2\text{O}/\text{phenol}$  ring ratio was increased. The heat change is constant but not zero because of a constant background heat. The heat flow at all points was found to be approximately constant, which suggests that there is no reaction heat other than the background heat, and consequently PEO 900 kDa and corilagin do not associate at  $30^\circ\text{C}$  in pure water.

Consequently these experiments verify the theoretical prediction that PEO and corilagin do not associate.

6.5.2  $^1\text{H}$  NMR

Only one peak was observed for the methylene protons of PEO in pure water. Compared with the pure PEO solution, the PEO proton signal in a PEO/corilagin solution ( $T = 293^\circ\text{K}$ ) did not significantly shift; 3.546 and 3.543 ppm respectively (Figure 7, left and right respectively). Moreover, there was no significant shift in the aromatic protons of corilagin when PEO was present.

Consequently, the  $^1\text{H}$  NMR results also support the theoretical prediction that PEO and corilagin do not associate, at room temperature, in the absence of salt.



**Figure 7** Experimental  $^1\text{H}$  NMR spectra of PEO ( $M_w = 0.9$  MDa) alone (left) and in the presence of corilagin (right) at room temperature, in  $\text{D}_2\text{O}$ , no salt added.

## 6.5.3 Absence of MCC flocculation

Papermaking experiments clearly show that, corilagin, PEO, as well as PEO/corilagin, do not flocculate MCC in pure water, because no changes in the apparent floc size (R) were detected with the PDA. The likely explanation of why no MCC flocculation occurred is that no PEO/corilagin complexes were formed in the first place. This is consistent with the theoretical prediction that PEO and corilagin do not associate, at room temperature, in the absence of salt. Only complexes can adsorb on MCC and bridge.

One possibility is that ions are involved in PEO/corilagin association and

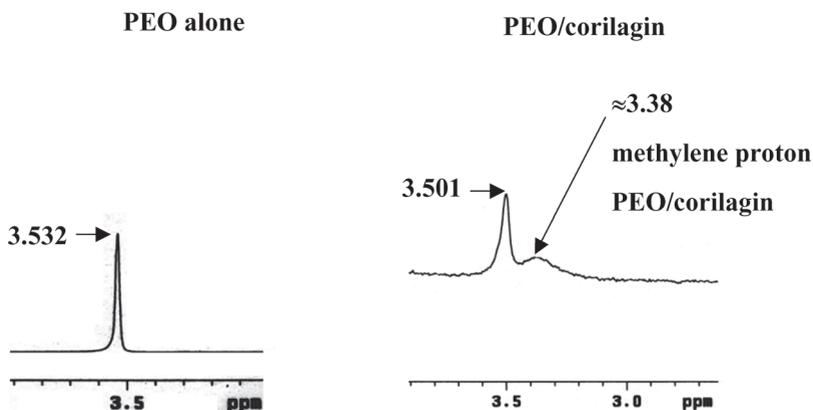
fibre fines flocculation, because salt is always present in fibre suspensions and often added to experiments as background electrolyte. Therefore it was decided to add salt to the system and to see whether or not this had any effect on the PEO/corilagin association.

## 6.6 PEO/corilagin association in the presence of salt

To introduce ions in the system in a controlled manner, 1 mM KCl was added to the PEO/corilagin solution. The PEO used in Figure 8 is a hydrophobically modified PEO, while the PEO used in Figure 7 is not hydrophobically modified. The difference of 0.014 ppm in the line signals is insignificant.

The PEO peak observed previously (Figure 7) broadened and slightly shifted, but more significantly a totally new second peak was observed at 3.38 ppm, arising from the PEO/corilagin complex formation (Figure 8). This agrees with the results of Cong et al. [12] for the PEO/PVPh-co-KSS complexes.

Consequently the ions of the salt are essential for the association of PEO and the cofactor corilagin.



**Figure 8** Experimental <sup>1</sup>H NMR spectra of PEO hydrophobically modified ( $M_w = 10$  MDa) alone (left) and in the presence of corilagin (right) in solution: 1 mM KCl, in  $D_2O$  at room temperature.

## 6.7 Flocculation of MCC

Before discussing the flocculation of MCC by PEO/corilagin in the presence of salt, the effect of salt alone has to be considered.

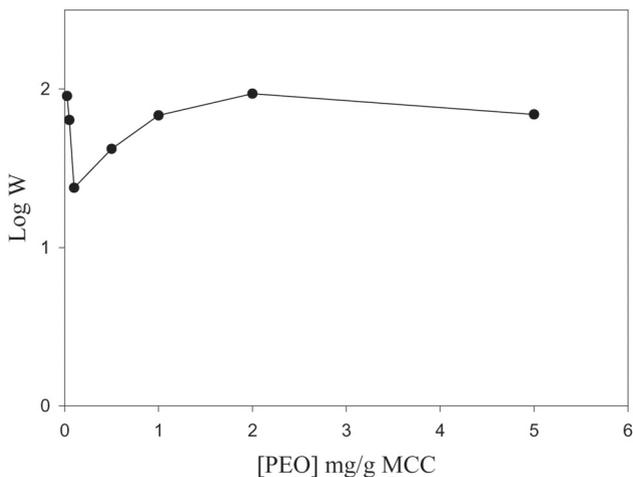
### 6.7.1 Salt-induced coagulation of MCC

The flocculation of MCC with salt follows classical behaviour with a critical coagulation concentration (CCC), defined as the minimal salt concentration that causes rapid coagulation of a dispersion [15], of 10 mM M KCl.

The experiments described in the next sections were carried out using a salt concentration of 1 mM KCl ( $\kappa^{-1} \cong 9.5$  nm). The value of  $k_{fast}$  from a 0.1 M KCl/MCC dispersion was used as the reference flocculation rate, to which the flocculation rate of MCC using PEO/corilagin can be compared.

### 6.7.2 Flocculation of MCC by PEO/corilagin/KCl

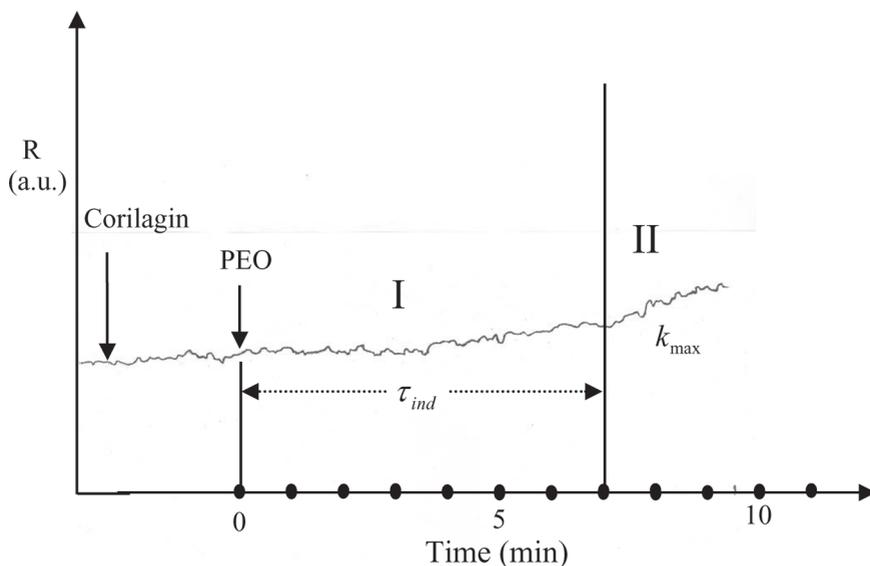
The results are expressed in terms of an apparent stability ratio  $W$ , because the MCC which was slightly coagulated by 1 mM KCl, showed additional flocculation when PEO was added. Consequently PEO must have shifted the dynamic equilibrium between floc formation and break-up, towards more floc formation. For all PEO/corilagin dosages, the rates of flocculation are slower than the fast rate (Figure 9).



**Figure 9** Apparent stability ratio  $W$  of MCC in the presence of PEO and corilagin. [MCC] = 300 mg L<sup>-1</sup>, Corilagin:PEO ratio = 1:1, [KCl] = 1mM.

From Figure 9, it can be seen that the optimum PEO/corilagin dosage, at which the flocculation rate is maximum ( $k_{\max}$ ), is at about 0.1 mg corilagin/g MCC [37].

Interestingly, the PEO/corilagin system shows an induction time ( $\tau_{ind}$ ), defined as the time between PEO addition and the time when the maximum flocculation rate ( $k_{\max}$ ) is reached (Figure 10).



**Figure 10** Changes in apparent MCC floc size ( $R$ ) as a function of time: 0.02 mg corilagin/g MCC,  $[MCC] = 300 \text{ mg L}^{-1}$ , corilagin:PEO ratio = 0.2:1,  $[KCl] = 1\text{mM}$ .

For the PEO:corilagin system, the change in the apparent MCC floc size follows an interesting pattern, which has two different regimes (Figure 10). During regime I slow flocculation occurs, while regime II is the flocculation period of maximum flocculation. In regime II, the maximum flocculation is reached, which does not change with time, as evidenced by a constant slope. Numerous data sets were obtained for the different experimental conditions and other cofactors, and Figure 10 can be considered a typical result [37].

The induction time period is increasing with PEO/corilagin concentration typically from 4 to 10 minutes, similar as observed for other cofactors [37]. If the induction period was due to the slow kinetics of PEO adsorption on

MCC, the induction time would decrease as a function of PEO/corilagin dosage. This not being the case, another possible explanation is that polymer rearrangement occurs on the surface of MCC.

Kinetic calculations were performed to explain these results [37]. The kinetics on real paper machine would be up to 1000 times faster. Consequently, the present conditions are much slower than real papermaking conditions.

### *6.7.3 Effect of corilagin:PEO ratio*

Corilagin:PEO ratios between 0.2 and 1 are optimum to flocculate MCC [37]. Lindström and Glad-Normark [2] showed that the optimum weight ratio of cofactor to PEO is about 1:1 for mixtures of fibres/MCC and fibres/latex. For latex flocculation, Xiao et al. [3] indicated that the optimum ratio for phenol formaldehyde resin (PFR):PEO is 1:1. This relationship holds also for copolymers, with long polyacrylamide (PAM) backbones and short polyethylene glycol (PEG) pendant chains, with molecular weight over three million [38].

It is interesting to note that all the cofactors [37] are negatively charged, but nevertheless flocculation occurs despite electrostatic repulsion between the complexes and complexes with MCC.

## **7 INTERACTIONS OF PEO AND CORILAGIN WITH ELECTROLYTE (SALT)**

Besides the fact that salt clearly affects the stability of MCC, two other possibilities should be more extensively studied: salt interacts with 1) PEO or 2) cofactor:

- 1) PEO: the presence of inorganic salts in aqueous solutions of PEO reduces the cloud point temperature (CPT), defined as the point where a phase separation between the PEO and water occurs [39, 40]. Various papers in literature describe the interactions between PEO and salts, but the results are not clearly understood [39–44].
- 2) Cofactor molecules can aggregate when the salt concentration is too high [45, 46], thus lowering the flocculation efficiency of PEO/cofactor systems.

## 8 PROPOSED MECHANISM

The present research shows that PEO and corilagin form a complex in the presence of 1 mM KCl. The PEO/corilagin complex formation is a necessary criterion for MCC flocculation, and hence the present results support the association induced polymer bridging mechanism [4] (Table 4).

**Table 4** Summary of the flocculation experiments. [MCC]= 300 mg L<sup>-1</sup>

| Flocculants   | KCl concentration (mM) | Flocculation |
|---------------|------------------------|--------------|
| PEO           | 0                      | NO           |
| Corilagin     | 0                      | NO           |
| PEO/Corilagin | 0                      | NO           |
| PEO           | 1                      | NO*          |
| Corilagin     | 1                      | NO*          |
| PEO/Corilagin | 1                      | YES**        |

\* No increase above salt induced coagulation.

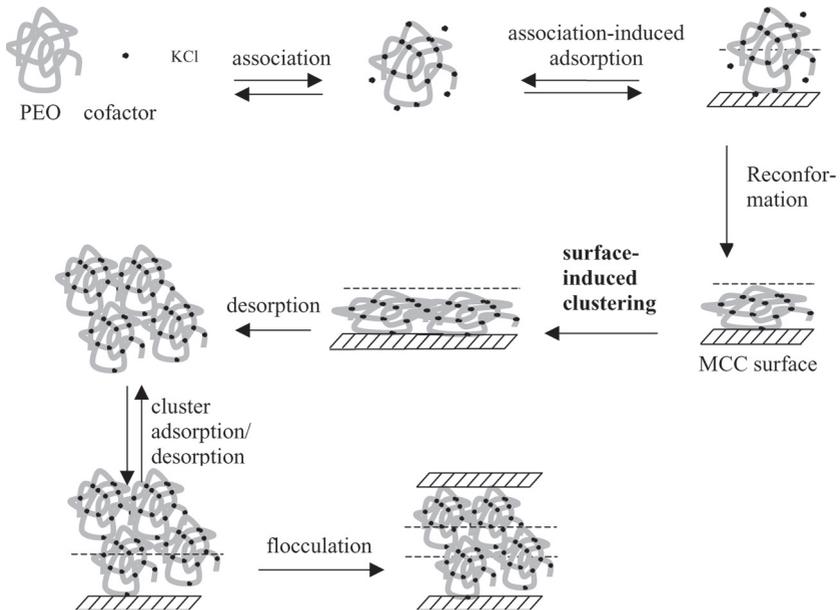
\*\* Substantial increase above the salt induced coagulation.

The corilagin cofactor is an example of a non-clustering cofactor: it does not cluster PEO in solution. Induction times are only observed for non-clustering cofactors.

To explain the induction time and subsequent MCC flocculation for non-clustering cofactors such as corilagin, the following mechanism is proposed: *surface-induced clustering coupled to association-induced polymer bridging* [32, 37].

The following sequence of events is believed to occur in PEO/corilagin/KCl induced flocculation of MCC (Figure 11).

- 1) PEO and corilagin associate to form a complex in the presence of salt (confirmed by <sup>1</sup>H NMR). Bulk clustering does not occur (confirmed by test tube and UV absorption experiments).
- 2) Adsorption of PEO/corilagin complexes on MCC surface, by the mechanism of association-induced adsorption.
- 3) Reformation and flattening of the complex, (common to nearly all polymer adsorption). Due to polymer flattening, the polymer adsorption layer becomes thinner than the diffuse double layer, resulting in a prevention of bridging flocculation by electrostatic repulsion.
- 4) Surface clustering, where single adsorbed association complexes entangle



**Figure 11** Schematics of proposed mechanism: association-induced polymer adsorption of PEO/corilagin on the surface of MCC, followed by surface induced clustering. The dashed lines represent the diffuse double layer thickness.

to form larger clusters (hypothesis required to explain observations). Indirect evidence is that the induction time increases with the PEO/corilagin dosage, and consequently is not kinetically driven.

- 5) Desorption of the surface clusters, due to the low affinity for MCC, followed by reformation in the bulk solution.
- 6) Cluster adsorption and desorption on the MCC surface, again due to low affinity of PEO to surface. Clusters adsorption results in thicker layers than for single molecules. Desorption ensures that bare surface areas exist, at low and high polymer concentration, which is needed for bridging flocculation.
  - a) If the reformation of clusters on the surface is faster than MCC flocculation, no flocculation occurs.
  - b) If clusters reformation is slower than MCC flocculation, flocculation of MCC occurs.

## 9 CONCLUDING REMARKS

Theoretical Semi-Empirical Molecular Orbital gas phase calculations (PM3) and Molecular Dynamics (MD) calculations in the presence of water, lead to the same surprising conclusion: no association between (PEO)<sub>6</sub> and corilagin occurs at room temperature. The reason is that the gain of association enthalpy is not large enough to overcome the loss in entropy.

For the association at low temperatures, the importance of hydrogen bonding was investigated. For example, corilagin has 9 phenolic groups (*R-OH*) and thus plenty of opportunity to hydrogen bond to the ether oxygen atoms in PEO. The Delocalized Molecular Orbitals (DLMOs) which cover the traditionally considered hydrogen bonds *R-OH...O* or *R-CH...O*, show a distinct “pinch”, a decrease of the electron density, between the *H...O* atoms. Even though bond lengths, bond angles, DLMO and electron densities for the PEO/corilagin complexes are consistent with the definition of hydrogen bonds, the number of inter-molecular *R-OH...O* and *R-CH...O* bonds does not correlate with the enthalpy of association, indicating that hydrogen bonding is not the driving force for complexation. Instead, the Semi-Empirical Molecular Orbital gas phase calculations (PM3) showed that the bonding mechanism is the sum of many small contributions of many delocalized molecular orbitals (DLMOs).

Unfortunately, the system we choose has only a weak tendency to form complexes. Nevertheless, several interesting conclusions can be drawn from the molecular modelling, as shown above.

PEO-corilagin interactions were experimentally studied by Isothermal Titration Calorimetry (ITC) and liquid state proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR). Isothermal titration calorimetry (ITC) shows that PEO and corilagin do not associate at 30°C in the absence of salt. The <sup>1</sup>H NMR results show no association between PEO and corilagin at room temperature in the absence of salt. The ITC and NMR results agree with gas phase PM3 and aqueous phase MD calculations which show that PEO/corilagin complexes do not form at room temperature in the absence of salt. Photometric Dispersion Analysis (PDA), shows the absence of flocculation of microcrystalline cellulose (MCC) by corilagin, PEO, as well as PEO/corilagin mixtures, which strongly suggests the absence of PEO/corilagin association. The association between PEO and corilagin in the presence of salt (KCl) has been confirmed by <sup>1</sup>H NMR. The stability ratios *W* (PDA) clearly show that PEO/corilagin induces MCC flocculation in the presence of salt. Consequently, salt is needed to induce MCC flocculation. The same has been observed for other cofactors, both clustering and non-clustering ones [32, 37].

For the non-clustering cofactors, such as corilagin, an induction time was observed, and a new salt dependent mechanism is proposed to explain the flocculation behaviour of MCC: *surface-induced clustering coupled to association-induced polymer bridging*. For such systems the clustering occurs on the surface, probably due to polymer interpenetration and entanglement.

In papermaking process water, there are a lot of salts that can trigger the PEO/cofactor association, which is a necessary condition to induce fibre fines flocculation. The reason why salt is required for PEO/cofactor complexation is currently under investigation.

One disadvantage of molecular modelling is that the calculations are time consuming, and require considerable skill in ensuring the accuracy of the results. Moreover, the results from molecular modelling should be validated with experiments. Nevertheless, we are confident that molecular modelling can be used to study other wet end papermaking systems, such as e.g. the complexation of cationic polyelectrolytes and dissolved anionic substances.

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## Transcription of Discussion

# MECHANISMS OF FLOCCULATION OF MICROCRYSTALLINE CELLULOSE BY POLY(ETHYLENE OXIDE) AND COFACTOR CORILAGIN

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*Tom Lindström*      STFI-Packforsk AB

I have a couple of questions. The first is the effect of salt. We also discovered the sensitivity of the system to electrolytes. We used aluminium to induce flocculation in the tannic acid/PEO system. Did you ever try other ions than the sodium or potassium?

*Roger Gaudreault*

Not at the moment because all the experiments were done in a condition where we tried to minimise the effect of other parameters and because the potassium ion has a good affinity for PEO. Because the charge density of aluminium ions is extremely high, it may induce additional effects, thus we used a monovalent ion to keep the system close to the simple model system. But the answer to your question is not yet.

## *Discussion*

*Tom Lindström*

I think the ion effect is something that is related to the gallic acid residue of the Corilagin. If you take, let us say, unbleached kraft pulp, or something like that, it will associate with PEO and then you block the phenolic groups (*e.g.* by methylation) then they do not get any PEO absorption. I think that is pretty straightforward, so I think this is something that is related to the gallic acid residue.

The second question is that in our work on network flocculation we point out the importance of collectors. You never use collectors on your side of the ocean. If you use collectors you get instantaneous network formation, which you do not get if you do not have a collector. The role of the collector is to collect the particles in the transient network. Have you ever tried that? I suggest you try it.

*Roger Gaudreault*

Not yet, but we will look at it. Thank you.