Thermodynamic Study of Polar Modifiers in the Equilibrium Staged Processes for the Styrene- Butadiene Rubber Processing

G. Ovejero, M. D. Romero, I. Díaz, E. Díez, J. Galán
Grupo de Catálisis y Procesos de Separación (CyPS)
Departamento de Ingeniería Química, Facultad de C. Químicas
Universidad Complutense de Madrid, Avda. Complutense s/n, 28040, Madrid, Spain

To analyze the behaviour of polar modifier in the separation steps of the synthetic rubber processing is necessary a thermodynamic study of these compounds with water, solvent and rubber. In this work, polymer-additive, solvent-additive and water-additive pairs were studied and measurements of vapor-liquid (VLE) and liquid-liquid equilibria (LLE) were carried out. The results of the thermodynamic modeling and steam stripping process simulations are presented herein.

1. Introduction

Styrene-butadiene rubbers (SBR) are mainly produced by a block polymerization process of monomers, catalyzed with alkyl lithium compounds in presence of an organic solvent (i.e cyclohexane). In a strongly non-polar media, the organometalic catalyst molecules tend to form oligomers by association with other ones. Therefore, polar modifier is added to the polymerization reactor in order to stabilize the alkyl lithium compounds improving the efficiency of the catalyst. Polar modifiers can also change other polymer properties as their microstructure and glass transition temperature (Hsu, 1997).These process additives, generally, have an hydrocarbon chain and an a polar domain, which perform chelant activity with the catalyst. A wide variety of compounds have been tried as polar modifiers, being ethers and amines the most widely studied (Qu, 2006; Halasa, 1999; Kerns, 2004). The work presented herein is focused in the behaviour of these compounds in the solvent separation step of rubber processing. In this way, some experimental data were obtained and a simulation tools based on ASPEN PLUS® commercial software, previously developed (Díez, 2008), was employed. In the simulation model, the stream from the polymerization reactor consisting of polymer and solvent goes to steam stripping process. Condensed bottom water is later separated from the final polymer by sedimentation whereas top steam carrying the solvent is condensed and two phases (aqueous and organic) are separated by decantation (Fig. 1).
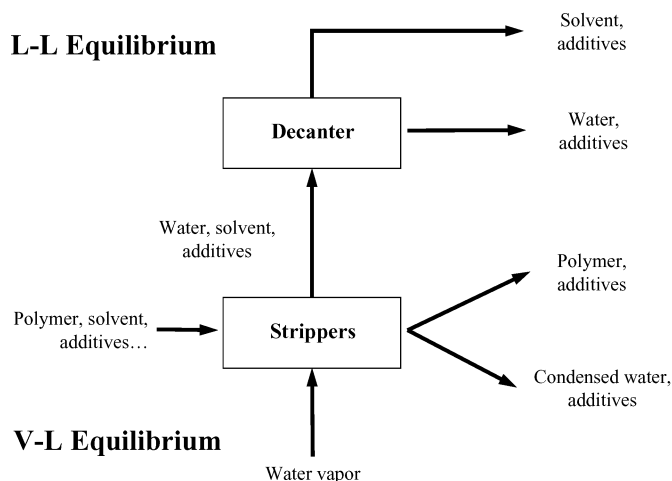
L-L Equilibrium

Figure 1 Steam stripping process scheme

In this work experimental equilibrium data (VLE or LLE) measurements of ethyl tetrahydrofurfuryl ether (ETE), triethyleneglycol dimethylether (TEGDME), N-N-N'-N' tetramethylethylene diamine (TMEDA), tetrahydrofurfurylamine (THFAM) and 4-ethylmorpholine (4EMORF) with both cyclohexane (CHEX) and water were obtained. In addition, the thermodynamic behaviour of other polar modifiers as 1,4 dioxane (DIOX), ethyleneglycol dimethylether (EGDME) and tetrahydrofuran (THF) were also studied from values of phase equilibria existing in ASPEN PLUS® database.

2. Experimental

2.1 Vapor-liquid equilibrium

All the experiments were performed using the isobaric ebullometric technique in the range of low additive compositions (the typical compositions used in the industrial process are below 1000 ppm). The apparatus has been previously used for similar purposes (Ovejero, 1992). In this apparatus, entirely made of glass, both the liquid and vapor phases are continuously recirculated in order to provide mixing of the phases and to ensure that equilibrium was established. The vapor condenser is connected to a constant-pressure system controlled by a Cartesian manostat. Pressure was kept constant at p = 101.32 kPa, with an accuracy of ±0.1 kPa. The equilibrium temperatures were measured with a certified thermocouple type J with an accuracy of ±0.1 °C. Both samples were analyzed with a Perkin-Elmer A/S gas chromatograph with a flame ionization detector. In this apparatus 4EMORF-cyclohexane, 4EMORF-water, THFAM-cyclohexane, THFAM-water, TEGDME-cyclohexane, TEGDME-water, TMEDA-cyclohexane and TMEDA-water equilibria were measured. In order to modeling VLE, a valid vapor pressure equation is needed. Parameters for Antoine expression of water, cyclohexane, ETE, TEGDME, TMEDA, THF, DIOX and EGDME are available in commercial databases (in this work ASPEN PLUS® database was used). However, THFAM and 4EMORF vapor pressure experiments were performed. The experiments were carried out in the ebullometer previously described by setting a

vacuum pump and a vacuum controller to vary pressure system. The pure substances were introduced into the ebullometer and then vacuum was set. The temperature of both vapor and liquid was measured after 30 min.

2.2 Liquid-liquid equilibrium

The ebullometric technique can be only used in homogeneous systems. If two liquid phases are present, then a simple stirred tank in a thermostatically controlled bath is needed. Thus, ETE-Water LLE measurements were performed. Consecutive additions of small quantities of ETE over a great amount of water were added until two phases were observed. Later on a sample of the aqueous phase was taken and analyzed by total organic carbon (TOC) measurements (SHIMAZDU VCSH).

3. Results

3.1 Thermodynamic modeling

All the data were fit to NRTL equation showing that this model is suitable to reproduce original data. In addition, UNIFAC predictions were also made. It can be seen that the higher the boiling point of the additive is, the worse the UNIFAC predictions are (THF<EGDME<DIOX<TMEDA<4EMORF<ETE<THFAM<TEGDME). In Figure 2: a-f bibliographic values of VLE for some light additives are presented and good UNIFAC predictions can be seen.

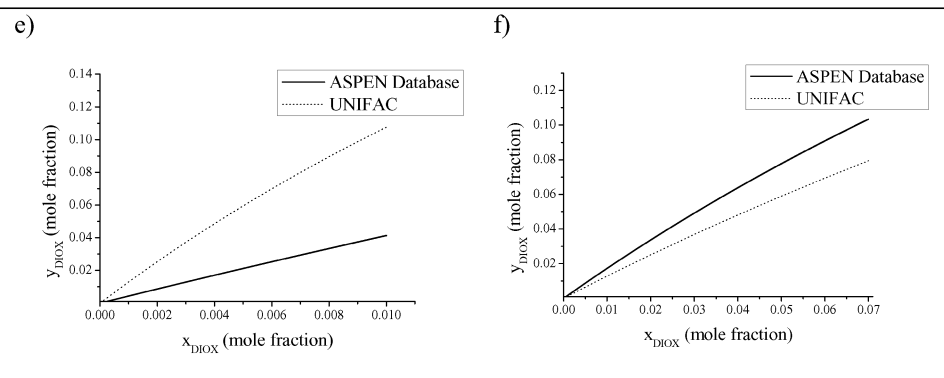| Additive-water systems	Additive-cyclohexane systems
a)	b)

c)   d)

e)

f)
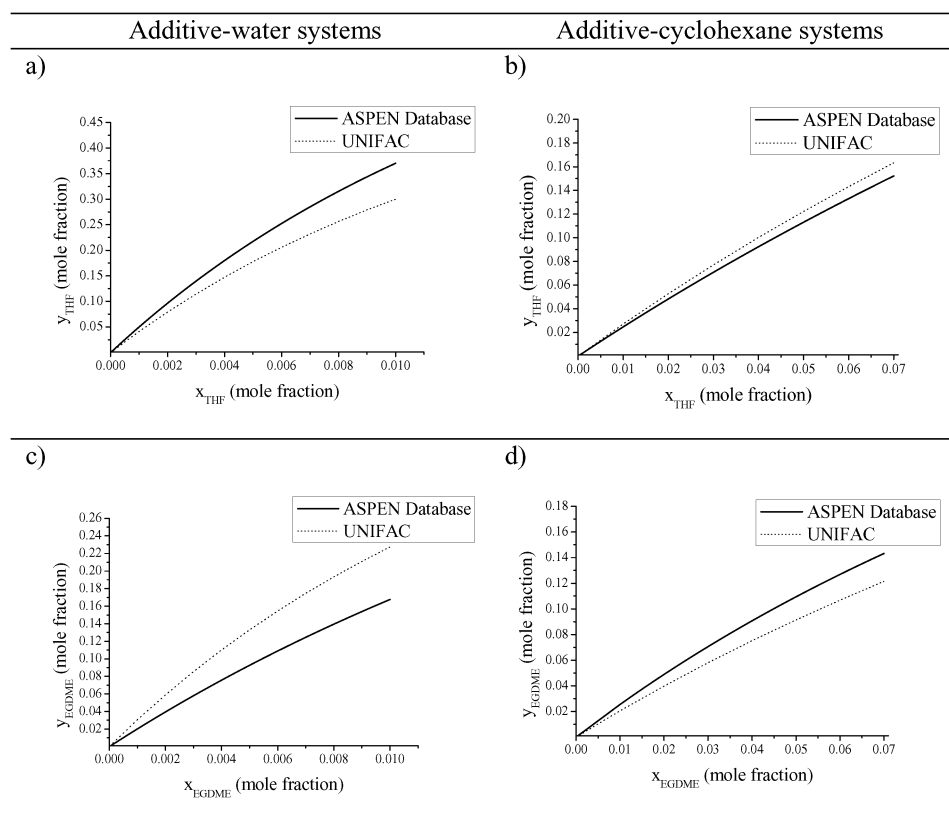
Figure 2 VLE bibliographic and predicted data at 101.32 kPa. a: THF-water; b: THF-cyclohexane; c: EGDME-water; d: EGDME-cyclohexane; e: DIOX-water; f: DIOX-cyclohexane.

On the other hand, heavy additive behaviours are, in general, difficult to predict for UNIFAC model as it is shown in Figure 3-i. In addition, it is observed that additive-water mixtures are even worse predicted than additive-cyclohexane ones. Therefore, it is necessary to obtain experimental data of VLE or LLE to get a reliable thermodynamic model when working with heavy polar modifier.

Additive-water systems	Additive-cyclohexane systems
a)	b)
c)	d)

e)

f)   g)

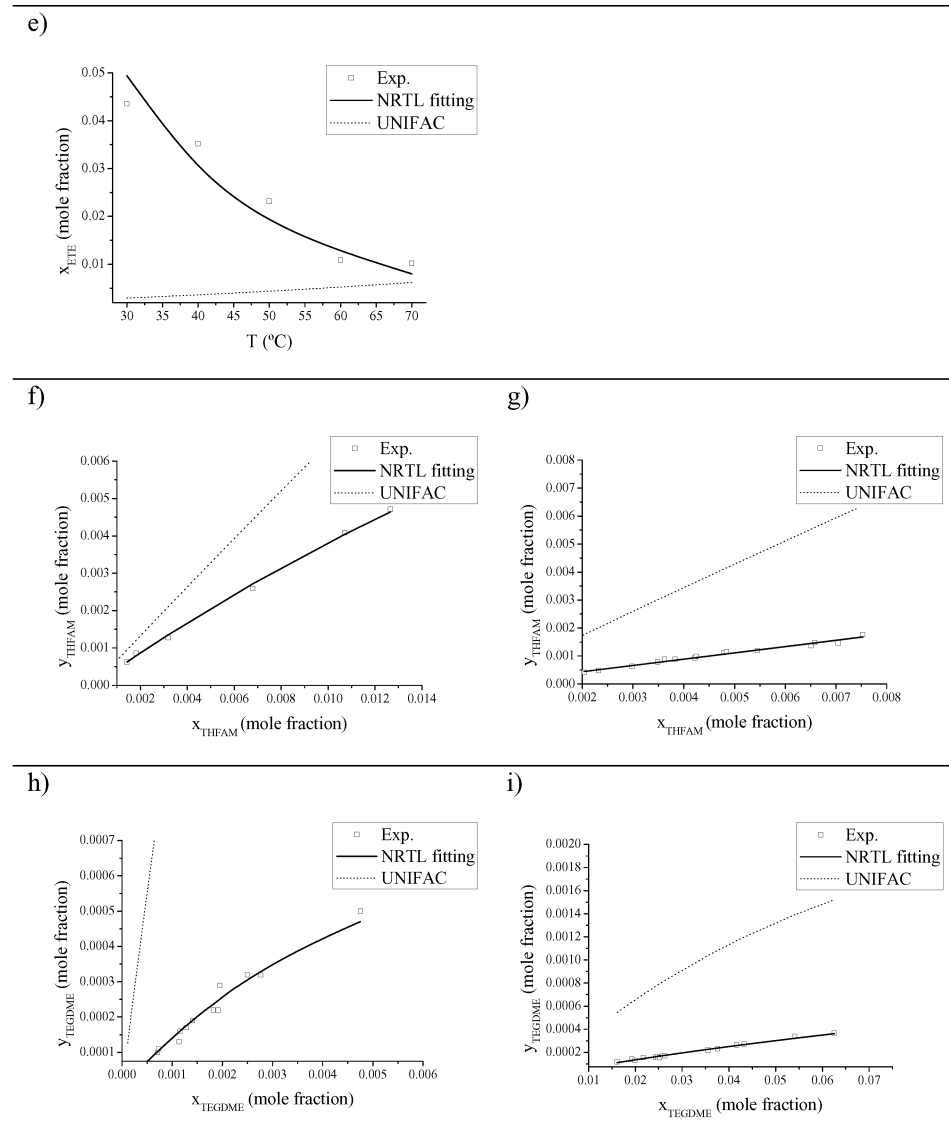h)   i)
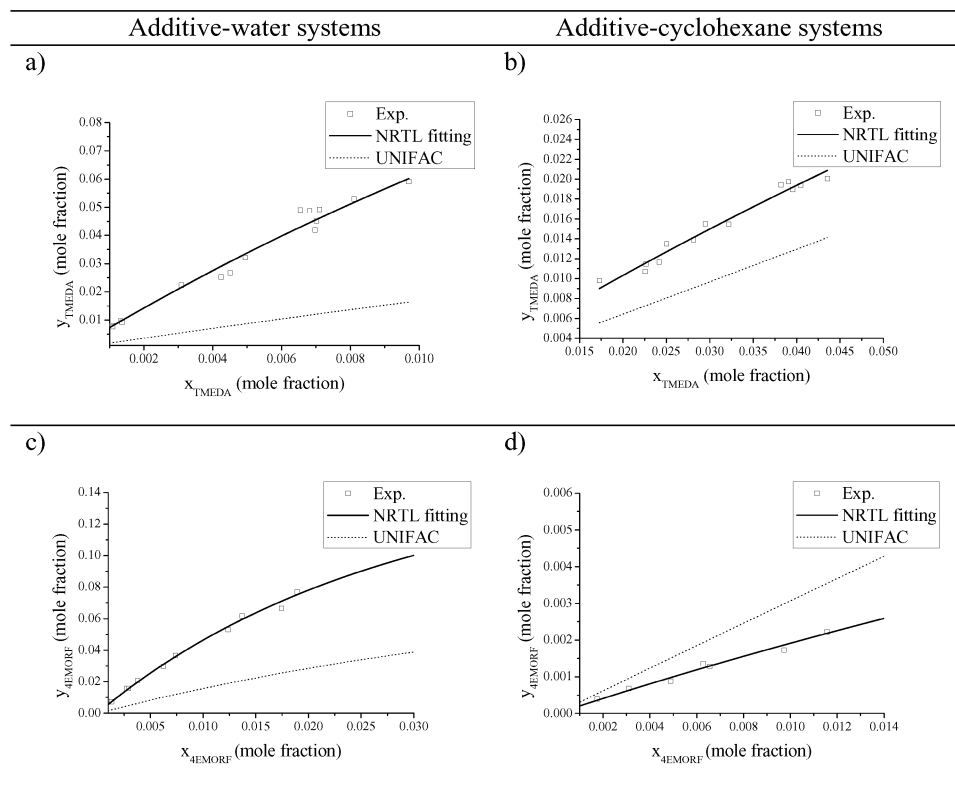
Figure 3 VLE and LLE experimental and predicted data of heavy polar modifiers at 101.32 kPa. a: TMEDA-water; b: TMEDA-cyclohexane; c: 4EMORF-water; d: 4EMORF-cyclohexane; e: ETE-water; f: THFAM-water; g: THFAM-cyclohexane; h: TEGDME-water; i: TEGDME-cyclohexane.

3.2 Simulation results

Table 1 quantify the distribution of the heavy polar modifiers in the different streams of the process as a function of the NRTL parameters employed (experimental fitting, UNIFAC predictions or literature values). The results are presented in terms of separation degree (mass flow of additive in the stream/mass flow of additive in the inlet

stream·100). As it can be seen, the results are very different when using UNIFAC parameters instead of the ones obtained by fitting experimental data.

Table 1 Simulation results of the stripping process for heavy polar modifiers

Additive	Add.-chex. model	Add.-water model	Final polymer	Solvent	Top water	Bottom water
TMEDA	Exp.	Exp.	0.6	80.8	11.1	7.5
	Exp.	UNIFAC	0.9	37.9	23.9	37.3
	UNIFAC	Exp	0.6	85.3	6.7	7.4
	UNIFAC	UNIFAC	0.9	45.0	16.8	37.2
4EMORF	Exp.	Exp.	0.8	79.4	8.6	11.2
	Exp.	UNIFAC	1.0	48.7	11.5	38.6
	UNIFAC	Exp	0.8	75.2	13.2	10.8
	UNIFAC	UNIFAC	1.0	44.1	16.4	38.4
ETE	Exp.	Exp.	n/a	n/a	n/a	n/a
	Exp.	UNIFAC	n/a	n/a	n/a	n/a
	UNIFAC	Exp	0.3	87.6	11.4	88.0
	UNIFAC	UNIFAC	0.6	94.9	2.1	2.5
THFAM	Exp.	Exp.	0.2	19.5	3.4	76.9
	Exp.	UNIFAC	0.3	28.6	3.3	67.8
	UNIFAC	Exp	0.2	10.7	11.8	77.3
	UNIFAC	UNIFAC	0.3	20.0	12.0	67.7
TEGDME	Exp.	Exp.	3.3	6.9	0.5	89.3
	Exp.	UNIFAC	6.9	16.9	0.3	75.9
	UNIFAC	Exp	3.3	5.0	0.5	91.2
	UNIFAC	UNIFAC	6.9	15.7	1.8	75.7

4. Conclusions

For the synthetic rubber processing is recommended to get experimental data of the equilibria where heavy polar additives are involved. UNIFAC predicts the behaviour of these substances properly only when they are light enough. Additive-water pair interactions seem to have a bigger influence than additive-cyclohexane over the simulation results. It can be due to hydrogen bonding that it is not taking into account by UNIFAC model.

5. References

Díez, E., 2008. Estudio termodinámico para simular los procesos de separación en una planta de síntesis de caucho. Ph D Thesis dissertation. Univ. Complutense Madrid.

Halasa, A F. et al., 1999. US Patent 5906956.

Hsu, W L. et al., 1997. Novel ether modifiers for anionic polymerization of isoprene. *Spring ACS Rubber Division Meeting*.

Kerns, M L. et al., 2004. US Patent 7074869.

Ovejero, G. et al., 1992. Vapor-liquid equilibria at 760 mmHg for the system vinyl acetate-n-decane. *J. Chem. Eng. Data*, 37, pp. 293–295.

Qu, B. et al., 2006. Structure of n-butLi in mixtures of ethers and diamines: influence of mixed solvation on 1,2-Additions to imines. *J. Am. Chem. Soc.*, 128, pp. 9355.