

# Evaluation of 1, 2 Propylene Glycol as a New Solvent for Aromatic Hydrocarbons Liquid-Liquid Extraction from Catalytic Reformer Products

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## Abstract

*There are few data in literature for the systems formed by the aromatic and paraffinic hydrocarbons with 1, 2 propylene glycol; current data do not allow evaluation of this solvent for aromatic hydrocarbons extraction from catalytic reformer products. The paper [1] presents: (1) Liquid-liquid experimental data in binary systems formed by 1, 2 propylene glycol with: benzene, n-hexane, toluene, n-heptane, methylbenzene, m-, o-, and p-xylene, n-octane; (2) Regression of experimental data in order to obtain NRTL and UNIQUAC binary interaction parameters for all binaries involved in aromatic extraction from catalytic reformer products. Present paper, based on [1] presents: (1) evaluating the performances of the new solvent; (2) the influence of introducing a co-solvent, water.*

**Keywords:** liquid-liquid extraction, cloud point, NRTL parameters, simulation

## Introduction

Since 2003, a study regarding the possible use of a 1, 2 propylene glycol (1, 2-propanediol) began in our department, having as a start point the similarity to other glycols in extractive distillation and liquid-liquid extraction. That certain solvent is synthesized in one of the Romanian petrochemical plants, with low costs. The first researches have shown remarkable performances for the extractive distillation of benzene from its mixture with n-hexane [2]. The experimental results for the liquid-vapor equilibrium have shown an important increase of the relative n-hexane-benzene volatility (up to 2.3). The simulation of the process has shown that the removing of the benzene up to a 50 ppm level is possible at reasonable costs. This promising beginning has encouraged us to profoundly study the liquid-liquid equilibrium.

The study should have the following stages:

- obtaining liquid-liquid equilibrium (LLE) data in the binary systems;
- the regression of the experimental data in order to obtain the binary interaction parameters for the NRTL model;
- evaluating the performances of the new solvent;
- the influence of introducing a co-solvent (water for example);

- the extraction of the aromatic hydrocarbons from a complex mixture using the new solvent (laboratory cell);

As it is commonly known, the processing of the liquid-vapor experimental data does not allow an appropriate estimation of the liquid-liquid equilibrium. At the opposite, the liquid-liquid equilibrium data allow a good evaluation of the liquid-vapor equilibrium.

The complex hydrocarbon fractions, that are exposed to liquid-liquid extraction in order to eliminate the aromatics, have an extremely different composition. The many components that are used make the study difficult. This is the reason why we have decided to study the liquid-liquid equilibrium in the concerned binaries, meaning the binaries that consist of 1, 2 propylene glycol (12PG) with the following hydrocarbons: n-hexane (NC6), benzene(B), n-heptane (NC7), toluene (T), n-octane (NC8), ethylbenzene (EB), o-xylene (OX), m-xylene (MX) and p-xylene (PX).

Since 2002, our bibliographical study has shown a growing interest for this solvent, up to 2007, when information appeared regarding the binary data created by 1, 2 propylene glycol with: benzene, n-hexane, n-heptane and toluene [3, 4, 5]. The PRO/II and ASPEN simulation softwares present the binary interaction parameters for the NRTL and UNIQUAC models [3, 4]. The paper [5] presents high errors in fitted NRTL parameters (more than 15%).

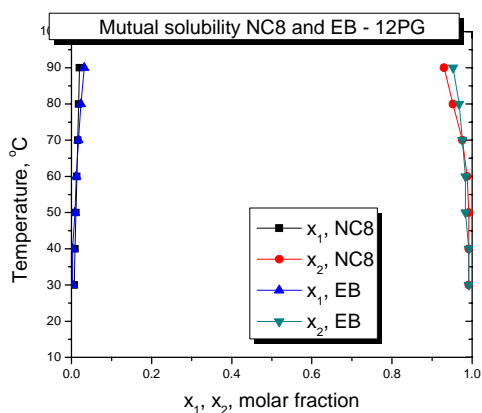
## Experimental

The LLE experimental data presented in [1] are obtained using a cell that determines the cloud point (own build, very simple), thermostated and fed with a precision burette. The used substances were chromatographic etalons, dried in zeolites. Each and every experimental point has been repeated until all possible errors were expelled (for three point at the same temperature no more 0.05% in molar concentration). The experimental data was then processed (fitted) in order to obtain the binary interaction parameters from the NRTL model.

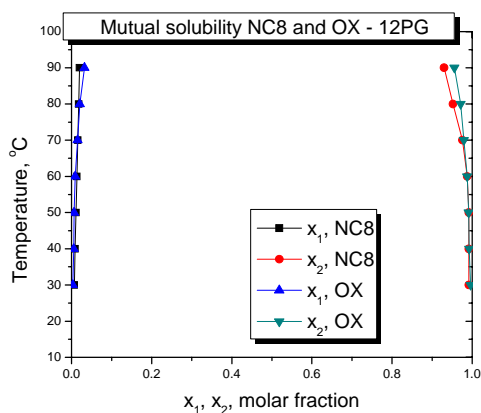
Starting with NC8, there can be found no data in the literature. All the following presented data in [1] are experimental. Maximum errors in fitted were 2%. The figure 1 ... 4 present experimental data only for C<sub>8</sub> hydrocarbons, namely only those systems not presented in present literature, but in our experimental.

The experimental data for each and every binaries has been regressed (fitted) in order to obtain the binary interaction parameters of the NRTL model. [1] presents the binary interaction parameters of the NRTL model for all the involved binaries.

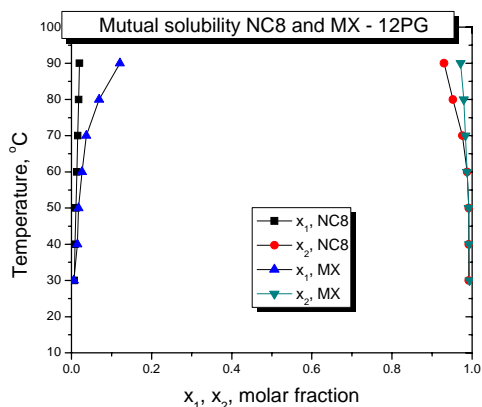
The both simulation programs [3, 4] present NRTL parameters for the systems water (W)-hydrocarbons and W-12PG. All these parameters [1, 3, 4] were used in simulations for evaluation of the new-solvent in the systems: mixture parafinic and aromatic hydrocarbon – 12PG and mixture parafinic and aromatic hydrocarbon – mixture W-12PG. The mixtures parafinic and aromatic hydrocarbon are formed by parafinic hydrocarbon and every aromatics for the same number of carbon atoms (C6 to C8). Every mixtures have the same concentration, 40% weight aromatics. The ratios solvent: hydrocarbons mixtures were fixed to 2:1 and 4: 1.



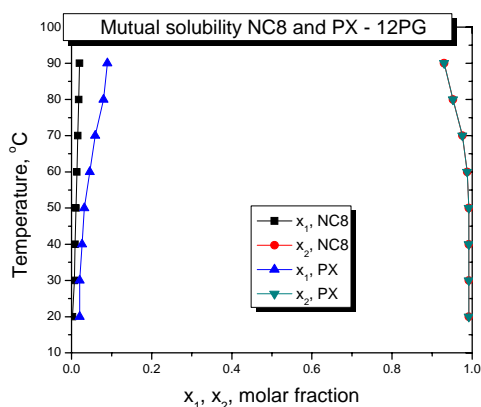
**Figure 1.** Comparative experimental ELL data for NC8 and EB with 12PG



**Figure 2.** Comparative experimental ELL data for NC8 and OX with 12PG



**Figure 3.** Comparative experimental LLE data for NC8 and MX with 12PG



**Figure 4.** Comparative experimental LLE data for NC8 and PX with 12PG

## Results and discussion

The simulation results (only for NC6-B-12PG, NC7-T-12PG and NC8-EB-12PG due of space reason) are presented in the table 1 ... 9. The phase one represents hydrocarbons phase and phase 2 is solvent phase.

**Table 1.** Simulation results for the system NC6-B-12PG for solvent ratio 2:1

	40°C		60°C		80°C		120°C	
	Molar fraction							
	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2
NC6	0.582	0.015	0.577	0.019	0.571	0.025	0.583	0.113
B	0.389	0.027	0.381	0.032	0.369	0.039	0.353	0.159
12PG	0.029	0.958	0.043	0.949	0.060	0.937	0.115	0.513
Total kmol	1/127	2.710	1.116	2.721	1.101	2.735	1.051	2.786

**Table 2.** Simulation results for the system NC6-B-12PG for solvent ratio 4:1

	40°C		60°C		80°C		120°C	
	Molar fraction							
	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2
NC6	0.605	0.015	0.604	0.020	0.603	0.025	0.604	0.041
B	0.367	0.026	0.356	0.030	0.341	0.036	0.300	0.050
12PG	0.028	0.959	0.040	0.950	0.056	0.939	0.096	0.909
Total kmol	1.012	5.453	0.973	5.491	0.922	5.543	0.762	5.703

**Table 3.** Simulation results for the system NC6-B-12PG-W for solvent ratio 2:1

	40°C		60°C		80°C		120°C	
	Molar fraction							
	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2
NC6	0.578	0.012	0.573	0.015	0.567	0.019	0.551	0.030
B	0.395	0.021	0.387	0.025	0.377	0.029	0.348	0.044
12PG	0.027	0.890	0.039	0.883	0.054	0.875	0.099	0.851
W	377 ppm	0.077	625 ppm	0.077	0.001	0.0077	0.003	0.076
Total kmol	1.145	2.861	1.139	2.867	1.132	2.874	1.107	2.900

**Table 4.** Simulation results for the system NC7-T-12PG for solvent ratio 2:1

	40°C		60°C		80°C		120°C	
	Molar fraction							
	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2
NC7	0.920	0.032	0.910	0.040	0.877	0.041	0.758	0.085
T	0.071	0.148	0.074	0.147	0.082	0.125	0.090	0.122
12PG	0.008	0.820	0.016	0.814	0.041	0.835	0.152	0.793
Total kmol	0.570	3.091	0.558	3.103	0.538	3.123	0.428	3.233

**Table 5.** Simulation results for the system NC7-T-12PG for solvent ratio 4:1

	40°C		60°C		80°C		120°C	
	Molar fraction							
	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2
NC7	0.947	0.018	0.935	0.024	0.913	0.032	0.801	0.068
T	0.043	0.071	0.044	0.071	0.046	0.071	0.050	0.070
12PG	0.011	0.910	0.021	0.905	0.041	0.898	0.149	0.862
Total kmol	0.520	5.764	0.494	5.795	0.454	5.836	0.234	6.050

**Table 6.** Simulation results for the system NC7-T-12PG-W for solvent ratio 2:1

	40°C		60°C		80°C		120°C	
	Molar fraction							
	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2
NC7	0.907	0.020	0.897	0.025	0.877	0.033	0.797	0.069
T	0.082	0.119	0.083	0.119	0.084	0.118	0.090	0.117
12PG	0.010	0.792	0.019	0.788	0.037	0.781	0.135	0.750
W	233 ppm	0.068	645 ppm	0.068	0.002	0.068	0.008	0.065
Total kmol	0.588	3.243	0.577	3.254	0.561	3.270	0.482	3.349

**Table 7.** Simulation results for the system NC8-EB-12PG for solvent ratio 2:1

	40°C		60°C		80°C		120°C	
	Molar fraction							
	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2
NC8	0.934	0.020	0.918	0.027	0.891	0.037	0.759	0.084
EB	0.055	0.115	0.062	0.114	0.069	0.112	0.085	0.109
12PG	0.011	0.865	0.020	0.860	0.040	0.851	0.156	0.807
Total kmol	0.498	3.033	0.484	3.046	0.463	3.067	0.337	3.193

**Table 8.** Simulation results for the system NC8-EB-12PG for solvent ratio 4:1

	40°C		60°C		80°C		120°C	
	Molar fraction							
	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2
NC8	0.960	0.016	0.946	0.021	0.922	0.030	0.802	0.067
EB	0.030	0.064	0.033	0.063	0.037	0.063	0.048	0.082
12PG	0.010	0.921	0.020	0.916	0.041	0.908	0.150	0.871
Total kmol	0.454	5.705	0.427	5.732	0.385	5.774	0.150	6.009

**Table 9.** Simulation results for the system NC8-T-12PG-W for solvent ratio 2:1

	40°C		60°C		80°C		120°C	
	Molar fraction							
	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2
NC8	0.931	0.015	0.917	0.021	0.982	0.029	0.771	0.068
EB	0.059	0.109	0.064	0.108	0.069	0.107	0.081	0.104
12PG	0.010	0.806	0.019	0.802	0.037	0.795	0.139	0.761
W	254 ppm	0.070	701 ppm	0.069	0.002	0.069	0.010	0.066
Total kmol	0.511	3.189	0.500	3.199	0.484	3.216	0.388	3.312

The simulation results (on base without solvent) show:

- low distribution coefficient of B between the two phases (1.57), but greater than NC6 (0.61);
- distribution coefficient of aromatics increased from B to EB: 10.33 for B and 14.75 for EB;
- separation power increased from B to EB: 2.56 for B, 65.81 for T and 114.67 for EB;

When the water is present in solvent the results show:

- distribution coefficient of aromatics increased from B to EB: 1.60 for B, 11.53 for T and 15.32 for EB;
- separation power increased from B to EB: 2.69 for B, 61.86 for T and 97.65 for EB.

The behaviour in presence of water is somewhat unusual; normally the separation power must increase in the presence of cosolvent. Future experimental study must validate this behaviour.

Concerning solving power the simulation results show:

- every mole of solvent solves 0.028 mole B and 0.016 mole NC6, 0.180 mole T and 0.039 mole NC7, 0.133 mole EB and 0.023 mole NC8 without water and 0.024 mole B and 0.013 mole NC6, 0.149 mole B and 0.025 mole NC7, 0.135 mole EB and 0.019 mole NC8. Again, unusual behaviour, solubility must decrease in presence of water.

## Conclusions

The paper presents, based on own experimental data (liquid-liquid equilibrium obtained for the binary systems with paraffinic or aromatics hydrocarbons and the new solvent, 1, 2-propanediol), the results of simulated liquid-liquid equilibrium in the systems paraffinic-aromatic-solvent, without and with water. Furthermore, this binary data should be confirmed in complete LLE experiments that use complex hydrocarbon mixtures.

## References

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## Evaluarea 1,2 propilen-glicolului ca solvent nou pentru extractia lichid-lichid a hidrocarburilor aromatice din produsele de reformare catalitică

### Rezumat

*Sunt puține date în literatură privind echilibrul lichid-vapori în sistemele formate de hidrocarburi (parafinice și aromatice) cu o nouă clasă de solvenți, propilenglicolii. Lucrarea prezintă, pe baza determinărilor experimentale și a regresiiilor efectuate în [1] evaluarea, performanțelor noului solvent, 1,2-monopropilen glicolul. Calculele au fost efectuate prin simulare pe amestecuri sintetice parafine-aromatice-solvent în domeniul C<sub>6</sub>-C<sub>8</sub>. De asemenea, tot prin simulare se evaluează influența apei utilizată drept co-solvent.*