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Liquid−Liquid Equilibria for *m*-Cresol + *o*-Toluonitrile + Hexane + Water + (Glycerol or Triethylene Glycol) at 313.15 K

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Liquid−liquid equilibria and separation factors for the systems *m*-cresol + *o*-toluonitrile + hexane + water + (glycerol or triethylene glycol) have been determined at 313.15 K in order to evaluate their suitability in separating *m*-cresol from *o*-toluonitrile. The effects of parameters such as the type of high-boiling solvent, solvent ratios, antisolvent ratios, and water to high-boiling solvent ratios on the separation of *m*-cresol from *o*-toluonitrile were investigated. These are illustrated on the basis of percentage of feed *o*-toluonitrile remaining in the high-boiling solvent phase and percentage recovery of *m*-cresol. From the experimental results it was concluded that triethylene glycol is more suitable for the proposed separation than glycerol.

Introduction

The recovery of valuable phenolic compounds from coal pyrolysis liquors has long been of interest. Cresols are the most prevalent of these compounds and typically account for 25%−45% of light and middle coal liquor distillates (Carlson and Christiansen, 1995).

The separation of the phenolic compounds from the neutral oils, also present in the pyrolysis liquors, is difficult owing to low relative volatilities and the formation of azeotropes and eutectics. (Fiege and Bayer, 1987) The separation of *m*-cresol and *o*-toluonitrile is especially difficult and cannot be achieved by means of distillation.

Separations of phenolic compounds from neutral oils by means of solvent extraction with solvents such as aqueous acetamide (Nair et al., 1967), sodium phenolate (Bizek et al., 1993), sodium xylenesulfonate, isobutyl acetate, and aqueous methanol solutions (Kodera et al., 1990) have been investigated. What count against these processes are high solvent ratios and complex postpurification of the cresol product.

Solvent extraction using high-boiling solvents, glycerol or triethylene glycol, a cosolvent, water, and an antisolvent, hexane, is proposed as an alternative separation process. In this study the feed to the extraction process is defined as a binary mixture of *m*-cresol and *o*-toluonitrile in the mass ratio 5:1.

Batch extraction tests were conducted to determine the effect of parameters such as types of solvents, solvent ratios, solvent mixtures, and antisolvents. Ratios of high-boiling solvent to feed, water to high-boiling solvent, and antisolvent to feed were varied and the resulting phases analyzed.

Experimental Section

Materials. Triethylene glycol, with a stated purity of 97% and *m*-cresol, with a stated purity of better than 98%, were purchased from Fluka. *o*-Toluonitrile, with a certified purity of better than 98%, was obtained from Aldrich Chemical Co. Glycerol, with a stated purity of 99.5%, was obtained from Saarchem. Analytical reagent grade hexane was obtained from NT Laboratories. All the chemicals were used without further purification. The water used was glass-distilled.

Apparatus. The batch extraction tests were carried out in standard 250 mL glass separating funnels, which were placed in a water bath. The water in the bath was circulated and kept at 313.15 K (±0.5 K) by means of a Haake D1 thermostat.

Procedure. Known masses, measured with a precision of ±0.001 g, of the pure components were separately added to the separating funnels. The separating funnels were shaken for 30 s and positioned in the water bath so that the level of the funnel contents was below the level of the water. The funnels remained in the bath for a minimum of 24 h. They were removed, shaken, and replaced at regular intervals.

Upon removal from the water bath, the high-boiling solvent (extract) and antisolvent (raffinate) phases were separately drained and stored in glass bottles with screw caps. The mass of each phase was measured with a precision of ±0.001 g and diluted to prevent secondary phase separation at ambient temperature. Samples of each phase were analyzed.

Binary solubility tests for the component pairs triethylene glycol, hexane and glycerol, hexane were carried out under the same conditions as the batch extraction tests, using the same experimental procedure and apparatus.

Care was taken throughout to minimize evaporation losses.

Analysis. The masses of *m*-cresol and *o*-toluonitrile in each of the resulting batch extraction phases were determined with a Varian 3400 gas chromatograph (GC) equipped with a flame ionization detector (FID) and a Hewlett-Packard 3394A integrator. A 60 m SGE BPX5 capillary column (inner diameter 0.32 mm) was used to get a good separation between the *m*-cresol and *o*-toluonitrile. The detector was calibrated using solutions of known concentrations. From material balances over each of the solutes, the accuracy of solute mass measurements in each phase was estimated to be within ±1.7% for *m*-cresol and ±1.2%

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for *o*-toluonitrile. Each analysis was repeated at least twice to ensure repeatability.

The long retention times needed for the separation of *m*-cresol and *o*-toluonitrile coupled with the thermal instability of the high-boiling solvents caused considerable fluctuation (±50%) in calibration response factors of the high-boiling solvents. This precluded direct high-boiling solvent analysis via gas chromatography. The concentrations of glycerol and triethylene glycol in the hexane phases and the hexane in the high-boiling solvent phases were thus estimated from solubility test data. The solubility test samples were analyzed on a Hewlett-Packard 5890A GC with an FID detector and HP 3393A integrator. An SGE BP1 capillary column was used. Using this column, the fluctuations in the high-boiling solvent response factors were reduced to ±5%. Each solubility sample was analyzed at least five times to ensure repeatability.

From material balances over each component, the accuracies of the measured concentrations of triethylene glycol and glycerol were estimated to be within ±0.9% and ±1.6%, respectively, for the solubility tests. The accuracy of the hexane measurements were estimated as being within 1.2% and 1.4%, respectively, for the solubility tests carried out with triethylene glycol and glycerol. The solubility data is shown in Table 1.

The water concentrations in each of the resulting batch extraction phases were determined by means of Karl Fischer volumetric titrations using a Metrohm E547 Automat. From mass balances, the accuracy of the measured water masses were estimated to be within 1.9%.

Results and Discussion

In most applications a prime concern is not only the ability of a solvent to extract the desired solute but also its ability to do so preferentially, thus affecting a degree of separation from other solutes that may be present. The selectivity of a solvent for solute *i* relative to *j* is measured by the separation factor β_{ij}, which is analogous to relative volatility in distillation.

$$\beta_{ij} = K_i/K_j$$

where K_i and K_j are the distribution coefficients of component *i* and *j*, respectively, and can be expressed as follows

$$K_i = x_i^{\mathrm{I}}/x_i^{\mathrm{II}}$$

where x_i^{I} and x_i^{II} are the equilibrium mass fractions of component *i* in the extract (high-boiling solvent) and raffinate (hexane) phases, respectively.

The distribution coefficient can have any value—even less than one—and the extraction will still be feasible. The higher the separation factor, the easier the liquid extraction will be (Cusack and Glatz, 1996).

The evaluation of the performance of the two high-boiling solvents is based on the recovery of *m*-cresol and the degree of separation of *m*-cresol from *o*-toluonitrile. The term feed is used for the binary mixture of *m*-cresol and *o*-toluonitrile, in the mass ratio 5:1, that is contacted with the solvents. The recovery of *m*-cresol is regarded as the mass percentage of the *m*-cresol that was fed to the batch extraction that remained in the high-boiling solvent phase. The recoveries are shown graphically in Figures 2, 4, and 6. The degree of separation achieved between *m*-cresol and *o*-toluonitrile is described both by means of *m*-cresol–*o*-toluonitrile separation factors as well as by the mass percentage of feed *o*-toluonitrile remaining in the high-boiling solvent phase. The separation factors are shown in Table 2. The percentage of *o*-toluonitrile remaining in the high-boiling solvent is shown graphically in Figures 1, 3, and 5.

Table 1. Mutual Solubility *S* of High-Boiling Solvents (A) and Hexane (B) at 40 °C

high-boiling solvent	*S*/(mass %) A in B	*S*/(mass %) B in A
triethylene glycol	0.80	1.31
glycerol	1.08	1.06

It can be seen from Table 2 that, whereas the *m*-cresol–*o*-toluonitrile separation factors obtained using triethylene glycol are typically greater than 10.0, the highest separation factor obtained with glycerol is 6.2. This can be attributed to the fact that, although the percentages of feed *o*-toluonitrile remaining in the high-boiling solvent phase are lower in the glycerol extractions than in the triethylene glycol extractions, the *m*-cresol recoveries achieved with glycerol are significantly lower than those achieved with the triethylene glycol at the same solvent and antisolvent to feed ratios. This is illustrated in Figures 2 and 4. For glycerol the *m*-cresol recoveries were in the range 61–77%, whereas it was above 91% for triethylene glycol.

It can be concluded from Table 2 that for both high-boiling solvents, an increase in the high-boiling solvent to feed ratio without exception leads to an increase in the *m*-cresol–*o*-toluonitrile separation factor at the same water to high-boiling solvent and hexane to feed ratios.

The effect of the high-boiling solvent to feed ratio on the percentage recovery of *m*-cresol and the percentage of feed *o*-toluonitrile remaining in the high-boiling solvent phase was found to be small in the case of the triethylene glycol extractions. The most significant effect was obtained with an increase in the high-boiling solvent to feed ratio from 2.0 to 3.0 at a constant water to solvent ratio of 0.33 and a hexane to feed ratio of 3.0. In this case an increase of only 1.3% in *m*-cresol recovery and a decrease of only 4.6% in the percentage *o*-toluonitrile remaining in the solvent phase were observed.

In the case of the glycerol extractions, the effect of the high-boiling solvent to feed ratio on the *m*-cresol recovery and the percentage of *o*-toluonitrile left in the high-boiling solvent phase was more significant. From Figures 5 and 6 it can be seen that an increase in the high-boiling solvent to feed ratio leads to a decrease in the percentage of feed *o*-toluonitrile remaining in the solvent phase and has little effect on the percentage recovery of *m*-cresol. For example, an increase in the glycerol to feed ratio from 0.5 to 1.0 leads to a 24.1% decrease in the percentage of feed *o*-toluonitrile remaining in the high-boiling solvent phase, while the percentage *m*-cresol recovery changed by less than 3.0%.

The effect of the water to high-boiling solvent and hexane to feed ratios on the separation efficiency is best illustrated by the percentage of feed *o*-toluonitrile remaining in the high-boiling solvent phase. In the case of triethylene glycol, an increase in the water to high-boiling solvent ratio, at constant high-boiling solvent to feed and hexane to feed ratios, leads to a significant decrease in the percentage *o*-toluonitrile remaining in the high-boiling solvent phase and has little effect on the *m*-cresol recovery. This is shown graphically in Figures 1 and 2. For instance, for a triethylene glycol to feed ratio of 1.0 and hexane to feed ratio of 5.0, an increase in the water to triethylene glycol ratio of 0.00 to 0.67 leads to a 30.7% decrease in the percentage *o*-toluonitrile recovered into the triethylene

Table 2. Isothermal Liquid–Liquid Equilibrium Data: High-Boiling Solvent Phase Mass Percentages x_i^{I}, Antisolvent Phase Mass Percentages x_i^{II}, and Separation Factors β_{12} for *m*-Cresol (1) + *o*-Toluonitrile (2) + High-Boiling Solvent (3) + Water (4) + Hexane (5) at 313.15 K and 101.3 kPa[a]

W/S	S/F	H/F	x_1^{I}	x_2^{I}	x_3^{I}	x_4^{I}	x_1^{II}	x_2^{II}	x_3^{II}	x_4^{II}	β_{12}
m-Cresol (1) + *o*-Toluonitrile (2) + Triethylene Glycol (3) + Water (4) + Hexane (5)											
0.67	1.0	5.0	31.22	2.56	39.05	26.66	1.15	1.95	0.77	0.028	20.8
0.67	1.0	1.0	30.29	5.12	38.51	25.57	1.92	3.05	0.76	0.029	9.4
0.11	1.0	3.0	38.87	5.51	49.10	5.87	1.29	1.96	0.77	0.056	10.8
0.33	1.0	5.0	35.56	3.60	44.84	15.40	1.25	1.71	0.77	0.022	13.5
0.67	0.8	3.0	34.99	4.31	34.91	25.34	1.62	2.42	0.77	0.035	12.2
0.67	1.0	3.0	33.26	3.96	30.70	31.67	1.65	2.43	0.77	0.035	12.4
0.33	2.0	3.0	22.42	2.63	55.36	18.85	0.76	2.28	0.77	0.010	25.7
0.33	3.0	3.0	16.62	2.06	60.15	20.37	0.41	2.21	0.78	0.018	43.5
0.00	2.0	3.0	26.54	3.78	68.76	0.00	0.74	2.20	0.77	0.000	20.8
0.00	1.0	5.0	43.41	5.01	50.91	0.00	1.15	1.46	0.78	0.000	11.0
1.00	1.0	3.0	26.83	3.21	34.31	35.19	1.24	2.28	0.77	0.014	15.3
m-Cresol (1) + *o*-Toluonitrile (2) + Glycerol (3) + Water (4) + Hexane (5)											
0.00	1.0	3.0	37.31	3.69	58.21	0.17	5.49	3.28	0.99	0.013	6.0
0.06	1.0	3.0	36.56	3.77	55.75	3.33	5.95	3.19	0.98	0.110	5.2
0.11	1.0	3.0	34.85	3.50	54.74	6.32	5.61	3.22	0.98	0.054	5.7
0.26	1.3	3.0	26.17	2.36	56.10	14.76	7.43	3.39	0.96	0.168	5.1
0.11	1.0	3.0	34.91	3.58	54.10	6.83	5.82	3.10	0.98	0.072	5.2
0.20	1.0	5.0	28.51	1.96	51.17	17.81	5.61	2.41	0.99	0.064	6.2
0.00	0.7	2.0	46.24	6.59	46.67	0.00	6.05	3.55	0.98	0.000	4.1
0.00	0.5	2.0	53.64	8.05	37.90	0.00	6.48	3.05	0.98	0.000	3.1
0.00	0.3	2.0	62.35	9.71	27.64	0.00	8.37	3.24	0.95	0.000	2.5
0.00	0.5	3.0	53.18	6.75	39.64	0.00	5.92	2.70	0.99	0.000	3.6
0.00	0.7	3.0	44.79	5.06	49.61	0.00	5.28	2.76	0.99	0.000	4.6
0.11	0.8	2.0	42.48	5.47	46.28	5.27	6.35	3.44	0.97	0.154	4.2
0.11	1.2	2.0	31.66	3.83	56.89	7.01	6.37	3.76	0.97	0.062	4.9
0.11	0.8	1.0	43.90	6.89	43.48	5.26	6.61	3.95	0.97	0.070	3.8
0.11	1.0	1.0	37.22	5.84	50.51	5.89	6.42	4.14	0.97	0.071	4.1
0.11	1.5	1.0	29.74	4.14	59.10	6.39	7.23	5.48	0.94	0.065	5.4
0.15	1.0	0.5	36.31	7.05	48.72	7.40	7.03	4.40	0.95	0.176	3.2
0.11	0.7	0.5	43.55	9.50	42.02	4.47	7.55	4.25	0.95	0.155	2.6
0.00	1.0	5.0	29.50	2.64	59.99	7.23	5.18	2.21	1.00	0.028	4.8
0.11	1.0	5.0	30.30	2.46	59.71	6.88	5.55	2.17	1.00	0.028	4.8
0.11	1.2	1.0	32.64	5.32	55.11	6.34	6.17	4.71	0.96	0.084	4.7

[a] W/S refers to the water to high-boiling solvent ratio, S/F to the high-boiling solvent to feed ratio, and H/F to the hexane to feed ratio.

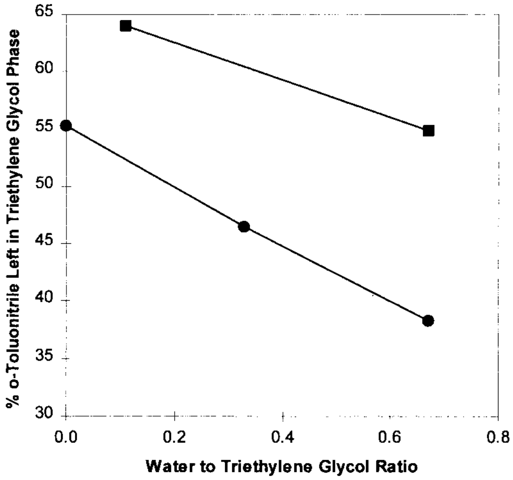

Figure 1. Effect of the water to triethylene glycol ratio on the mass percentage of feed *o*-toluonitrile remaining in the triethylene glycol phase at a constant solvent to feed ratio of 1.0: ■, hexane to feed ratio = 3.0; ●, hexane to feed ratio = 5.0 (mass ratios).

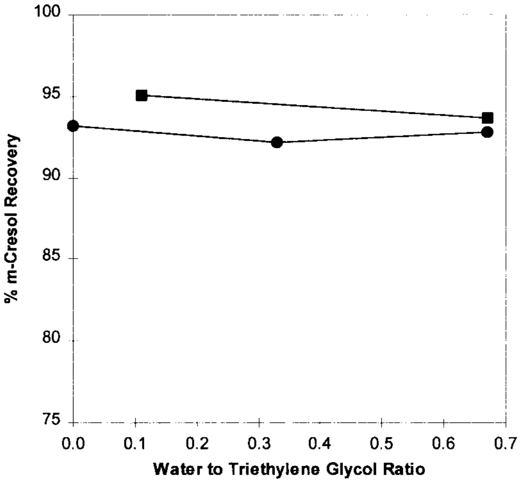

Figure 2. Effect of the water to triethylene glycol ratio on the mass percentage recovery of feed *m*-cresol at a constant triethylene glycol to feed ratio of 1.0: ■, hexane to feed ratio = 3.0; ●, hexane to feed ratio = 5.0 (mass ratios).

glycol phase, while the percentage *m*-cresol recovered changed by less than 2%.

In the case of the glycerol extractions, the water to high-boiling solvent ratio has a negligible effect on both the percentage *o*-toluonitrile remaining in the high-boiling solvent phase and the percentage *m*-cresol recovery and consequently has no effect on the separation factors. This is shown graphically in Figures 3 and 4.

It can also be seen from Figure 1 that an increase in the hexane to feed ratio leads to a considerable decrease in the percentage *o*-toluonitrile remaining in the high-boiling solvent phase. For instance, for triethylene glycol, at a constant water to triethylene glycol ratio of 0.67, an increase in the hexane to feed ratio from 3.0 to 5.0 leads to a 30.2% decrease in the percentage *o*-toluonitrile remaining. The corresponding decrease in *m*-cresol recovery is only 1.1%.

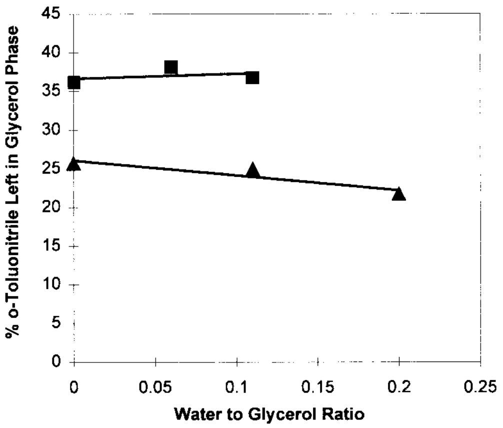

Figure 3. Effect of the water to glycerol ratio on the mass percentage of feed *o*-toluonitrile remaining in the glycerol phase at a constant solvent to feed ratio of 1.0: ■, hexane to feed ratio = 3.0; ●, hexane to feed ratio = 5.0 (mass ratios).

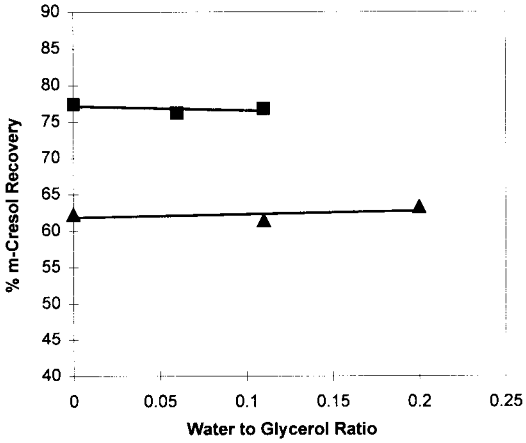

Figure 4. Effect of the water to glycerol ratio on the mass percentage recovery of feed *m*-cresol at a constant glycerol to feed ratio of 1.0: ■, hexane to feed ratio = 3.0; hexane to feed ratio = 5.0 (mass ratios).

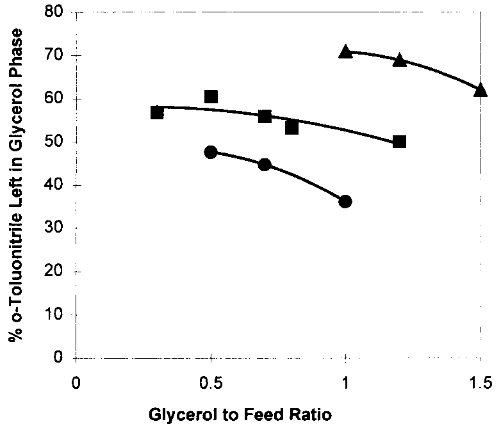

Figure 5. Effect of the glycerol to feed ratio on the mass percentage of feed *o*-toluonitrile remaining in the glycerol phase: ▲; hexane to feed ratio = 2.0, water to glycerol ratio = 0.0; ■, hexane to feed ratio = 1.0, water to glycerol ratio = 0.11; ●, hexane to feed ratio = 3.0, water to glycerol ratio = 0.0 (mass ratios).

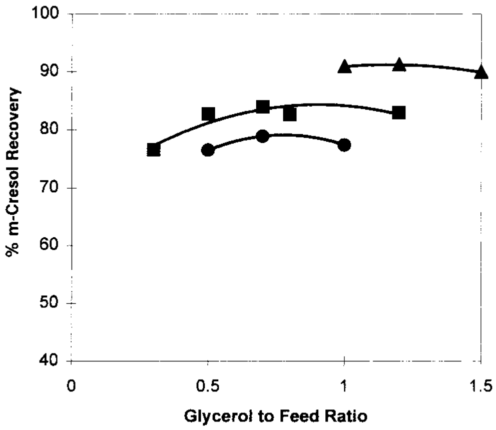

Figure 6. Effect of the glycerol to feed ratio on the mass percentage recovery of *m*-cresol: ▲, hexane to feed ratio = 2.0, water to glycerol ratio = 0.0; ■, hexane to feed ratio = 1.0, water to glycerol ratio = 0.11; ●, hexane to feed ratio = 3.0, water to glycerol ratio = 0.0 (mass ratios).

For the glycerol extractions, both the percentage *o*-toluonitrile remaining as well as the percentage *m*-cresol recovery decrease significantly with an increase in the hexane to feed ratio. From Figures 3 and 4 it can be seen that for constant water to glycerol ratios of 0.00 the percentage *o*-toluonitrile remaining decreases by 29.0% while the percentage *m*-cresol recovery decreases by 19.6% as the hexane to feed ratio increases from 3.0 to 5.0. For a glycerol to water ratio of 0.11, the percentage *o*-toluonitrile remaining decreases by 32.2%, while the percentage *m*-cresol recovery decreases by 20.0% as the hexane to feed ratio increases from 3.0 to 5.0.

Conclusions

Liquid−liquid equilibria and separation factors for the systems *m*-cresol + *o*-toluonitrile + hexane + water + (glycerol or triethyleneglycol) have been determined at 313.15 K in order to evaluate their suitability in separating *m*-cresol from *o*-toluonitrile.

An increase in the high-boiling solvent to feed ratio leads to an increase in the *m*-cresol−*o*-toluonitrile separation factors for glycerol and triethylene glycol.

In the case of triethylene glycol extractions, an increase in either the water to high-boiling solvent ratio or the hexane to feed ratio leads to a decrease in the percentage *o*-toluonitrile remaining in the high-boiling solvent phase and has no significant effect on the *m*-cresol recovery.

In the case of the glycerol extractions, an increase in the water to high-boiling solvent ratio has a negligible effect on both the percentage *o*-toluonitrile remaining and the *m*-cresol recovery, while an increase in the hexane to feed ratio leads to considerable decreases in both the percentage *o*-toluonitrile and percentage *m*-cresol remaining in the high-boiling solvent phase.

On the basis of *m*-cresol-*o*-toluonitrile separation factors, it can be concluded that triethylene glycol separates *m*-cresol from *o*-toluonitrile more efficiently than does glycerol. Furthermore, the percentage *m*-cresol recovered with glycerol is unacceptably low when compared to the recoveries achieved with triethylene glycol.

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