Liquid–Liquid Equilibria for Separation of Toluene from Heptane by Benzyl Alcohol Tri(ethylene glycol) Mixtures

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The solubilities for the binary systems (1) toluene/tri(ethylene glycol), (2) heptane/tri(ethylene glycol), and (3) heptane/benzyl alcohol are reported. Data for two ternary systems, toluene/heptane/tri(ethylene glycol) and toluene/heptane/benzyl alcohol, are given, and finally toluene/heptane/benzyl alcohol/tri(ethylene glycol) has been investigated. This last system affords a consolute point system, and it is possible to cause separation of benzene from heptane by producing a homogeneous phase at 60 °C and then cooling to 40 °C to produce a two-phase system.

Introduction

Aromatic fractions can be recovered from aromatic–aliphatic mixtures with use of a variety of chemicals by classical liquid–liquid extraction methods. An alternative method would be that where a consolute temperature system is used (*1*). In this last method a binary system of chemicals can be contacted at one temperature when a homogeneous phase results, and then when the temperature is changed, two phases result and solutes will distribute between these phases. This method of distribution thus involves a "temperature swing".

Examples of consolute systems are given by Francis (*2*), who reports the lower critical solution temperature (LCST) and upper critical solution temperature (UCST). In this system, benzyl alcohol and toluene are reported to be mutually soluble but the binary system of benzyl alcohol and heptane has an *upper critical solution temperature* (*2*).

Tri(ethylene glycol) is used in the separation of aromatics (*3*). However, the liquid–liquid equilibrium data of the ternary system containing tri(ethylene glycol), toluene, and heptane have been reported.

The present work reports the solubilities of toluene and heptane in tri(ethylene glycol) and heptane in benzyl alcohol and the liquid–liquid extraction data for two ternary systems, tri(ethylene glycol), toluene, and heptane and benzyl alcohol, toluene, and heptane, and the quaternary system tri(ethylene glycol), benzyl alcohol, toluene, and heptane. Separation factors for heptane and toluene are also reported.

Experimental Section

Materials. The *n*-heptane, toluene, and benzyl alcohol were supplied by BDH Ltd., having purities of 99.5%, 99.95%, and 99%, respectively. The tri(ethylene glycol) is technical grade with 98.9% purity, obtained from Imperial Chemical Industries Ltd. These chemicals were used without further purification.

Procedure. The solubilities and the binodal curves were determined by the cloud-point method and the tie lines by analysis of the resulting mixtures.

The cloud-point method used in the present work includes two approaches, i.e. use of constant-temperature or constant-composition techniques. For a determination of solubilities and binodal curves at 25 °C, the homogeneous samples of known compositions were titrated in a thermostated glass-stoppered flask to the appearance of turbidity. The amount of components added was determined by weighing before and after titration. For the data at the temperatures other than 25 °C, the heterogeneous samples of known total compositions were heated to make them homogeneous and then cooled step by step until the cloud point appeared. The temperature was measured to within ±0.1 °C.

The tie lines were obtained by analysis of mixtures on a gas chromatograph, Perkin-Elmer Model 8700. A flame ionization detector was used with a Reoplex (2% on chromosorb) column of 2 m in length. The mixtures of known total compositions, contained in glass-stoppered flasks, were maintained at the required temperature in a thermostat. Repeated shaking of the flasks occurred over a period of more than 2 h.

Because the test temperature was higher than the ambient temperature, the samples for analysis were dissolved in a solvent (pentanol) to prevent premature separation.

The sensitivity of the chromatograph to tri(ethylene glycol) was poor, so the analysis of samples containing tri(ethylene glycol) included two steps. First, the toluene, heptane, and benzyl alcohol content was determined. If there was no benzyl alcohol in the samples, it was necessary to add it as an internal standard. Then, the ratio of benzyl alcohol to tri(ethylene glycol) was determined. The content of tri(ethylene glycol) was then calculated from the known content of benzyl alcohol.

A comparison of the two analytical methods, i.e. cloud point and GLC, can only be made for the ternary system. As seen in Figure 4, the points from the two methods agree very well except near the top of the curve, in this region the cloud point method becomes difficult because of a blue color that developed in the mixture.

Table I. Solubilities of Heptane (1) in Benzyl Alcohol (2) (Mole Fraction)

x_1	x_2	temp, °C	x_1	x_2	temp, °C
0.1841	0.8159	25.0	0.5484	0.4516	51.4
0.1858	0.8142	28.6	0.5747	0.4253	51.2
0.2025	0.7975	32.8	0.5758	0.4242	51.2
0.2672	0.7328	43.0	0.6259	0.3741	51.0
0.3128	0.6872	47.5	0.6722	0.3278	49.5
0.3162	0.6838	47.9	0.7321	0.2679	47.2
0.4115	0.5885	51.0	0.8459	0.1541	36.8
0.4235	0.5765	51.1	0.8929	0.1071	26.0
0.4884	0.5116	51.3	0.9025	0.0975	25.0
0.5134	0.4866	51.5			

Table II. Solubilities of Heptane (1) in Tri(ethylene glycol) (2) (Mole Fraction)

x_1	x_2	temp, °C	x_1	x_2	temp, °C
0.9997	0.0003	25.0	0.9949	0.0051	50.4
0.9989	0.0011	30.1	0.0373	0.9637	51.6
0.9985	0.0015	35.2	0.0272	0.9728	38.9
0.9979	0.0021	38.7	0.0191	0.9809	25.0
0.9964	0.0036	45.6			

Results

The experimental data for the solubilities of heptane in benzyl alcohol and heptane and toluene in tri(ethylene glycol) are given

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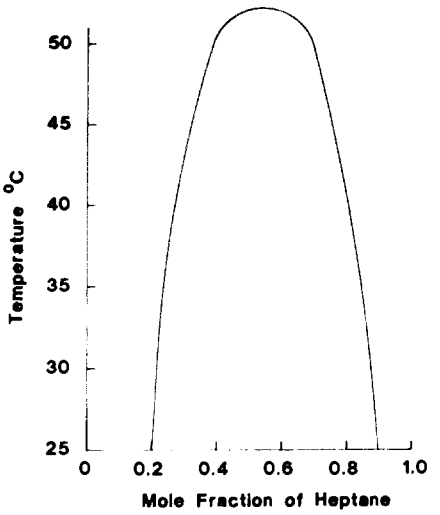

Figure 1. Solubility curve for heptane in benzyl alcohol.

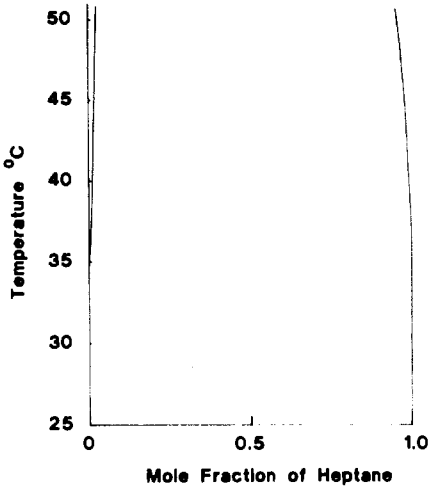

Figure 2. Solubility curve for heptane in tri(ethylene glycol).

Table III. Solubilities of Toluene (1) in Tri(ethylene glycol) (2) (Mole Fraction)

x_1	x_2	temp, °C	x_1	x_2	temp, °C
0.9874	0.0126	25.0	0.3798	0.6202	47.2
0.9855	0.0145	26.8	0.3716	0.6284	44.9
0.9805	0.0195	31.8	0.3639	0.6361	39.5
0.9768	0.0232	34.6	0.3561	0.6439	33.0
0.9689	0.0311	38.9	0.3478	0.6522	25.0

Table IV. Solubilities in the Ternary System of Toluene (1), Heptane (2), and Benzyl Alcohol (3) at 25 °C (Mole Fraction)

x_1	x_2	x_3	x_1	x_2	x_3
0.0000	0.9025	0.0975	0.1050	0.3791	0.5159
0.0746	0.7155	0.2099	0.0959	0.3720	0.5321
0.1038	0.6024	0.2938	0.0873	0.2886	0.6241
0.1189	0.5515	0.3296	0.0735	0.2476	0.6789
0.1163	0.5078	0.3759	0.0253	0.1974	0.7773
0.1105	0.4920	0.3975	0.0000	0.1841	0.8159
0.1074	0.4585	0.4343			

in Tables I–III, and the solubility curves are shown in Figures 1–3. The binary system of heptane and benzyl alcohol has a UCST of 51.5 °C (*4*). This UCST was reported by A. W. Francis as 50.6 (*4*) and 60 °C (*2*). It would appear that the last value was measured by Francis and accepted to be the *true* value. It should be noted that this UCST is measured only with difficulty due to the solution showing a light blue color near to the UCST.

The data for the binodal curve of the ternary system of toluene, heptane, and benzyl alcohol at 25 °C are listed in Table IV, and the tie line data, indicating the compositions of the two phases at equilibrium, are reported in Table V. The binodal curve and tie lines are plotted in Figure 4. This last figure indicates that the data for the binodal curve and tie lines are consistent except near the top of the binodal curve. Any errors

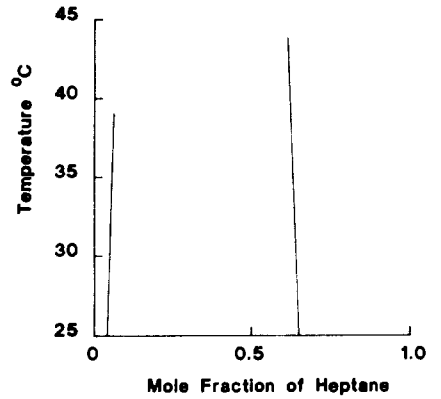

Figure 3. Solubility curve for toluene in tri(ethylene glycol).

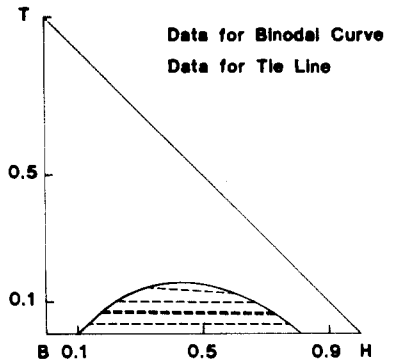

Figure 4. Binodal curve on tie line for the ternary system toluene, heptane, and benzyl alcohol.

are again due to the difficulties with the blue color of the solutions in this region.

The tie lines and their data for the ternary system of toluene, heptane, and tri(ethylene glycol) are given in Table VI and Figure 5.

Table V. Tie Line Distribution Coefficient and Selectivity Data for the System of Toluene (1), Heptane (2), and Benzyl Alcohol (3) at 25 °C

heavy-phase mole fraction			light-phase mole fraction			distribution coefficient		
x_1	x_2	x_3	x_1'	x_2'	x_3'	toluene	heptane	selectivity
0.0145	0.1799	0.8056	0.0253	0.8585	0.1162	0.5731	0.2096	2.73
0.0476	0.2115	0.7409	0.0659	0.7476	0.1865	0.7223	0.2829	2.55
0.0509	0.2196	0.7295	0.0713	0.7325	0.1962	0.7139	0.2998	2.44
0.0671	0.2425	0.6904	0.0818	0.6970	0.2212	0.8203	0.3479	2.36
0.0801	0.2765	0.6434	0.0943	0.6518	0.2539	0.8494	0.4242	2.00
0.0812	0.2781	0.6407	0.0958	0.6457	0.2585	0.8476	0.4307	1.97
0.0976	0.3213	0.5811	0.1132	0.5708	0.3160	0.8622	0.5636	1.53

Table VI. Tie Line Distribution Coefficient and Selectivity Data of the System of Toluene (1), Heptane (2), and Tri(ethylene glycol) (3) at 25 °C

heavy-phase mole fraction			light-phase mole fraction			distribution coefficient		
x_1	x_2	x_3	x_1'	x_2'	x_3'	toluene	heptane	selectivity
0.2496	0.0101	0.7493	0.7859	0.2049	0.0092	0.3061	0.0493	6.21
0.2268	0.0105	0.7627	0.7341	0.2597	0.0062	0.3089	0.0405	7.63
0.1955	0.0126	0.8029	0.6297	0.3660	0.0043	0.3105	0.0344	9.03
0.1643	0.0130	0.8227	0.5134	0.4836	0.0030	0.3200	0.0269	11.90
0.1584	0.0133	0.8283	0.4930	0.5045	0.0025	0.3213	0.0264	12.17
0.1116	0.0162	0.8722	0.3117	0.6870	0.0013	0.3580	0.0236	15.17
0.0820	0.0175	0.9005	0.2126	0.7865	0.0009	0.3857	0.0223	17.30
0.0271	0.0182	0.9547	0.0649	0.9346	0.0005	0.4176	0.0195	21.42

Table VII. Data for the Binodal and Phase Boundary Curve of Quaternary System (1): Pseudocomponent 1 Containing 20 mol % Tri(ethylene glycol) and 80 mol % Benzyl Alcohol and Pseudocomponent 2 Containing 50 mol % Toluene and 50 mol % Heptane

x_1	x_2	temp, °C	x_1	x_2	temp, °C
0.7770	0.2230	37.0	0.4169	0.5831	45.3
0.7491	0.2509	41.5	0.3527	0.6473	45.6
0.7002	0.2998	43.5	0.3236	0.6764	45.8
0.6949	0.3051	44.0	0.2894	0.7106	46.8
0.6538	0.3462	46.7	0.2186	0.7814	48.0
0.6254	0.3746	47.8	0.1967	0.8033	47.9
0.6439	0.3561	46.8	0.1836	0.8162	47.8
0.5782	0.4218	48.9	0.1630	0.8370	47.6
0.5557	0.4443	48.9	0.1500	0.8500	47.1
0.5392	0.4608	48.4	0.1299	0.8701	45.3
0.4965	0.5035	47.2	0.1105	0.8895	45.2
0.4704	0.5296	46.3	0.0832	0.9168	43.6

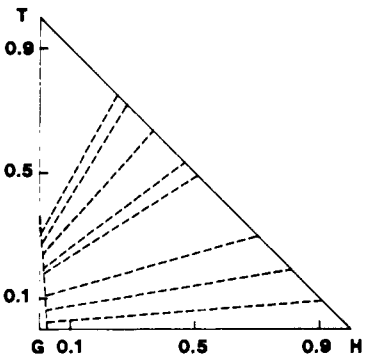

Figure 5. Tie line for the ternary system toluene, heptane, and tri(ethylene glycol).

In Tables V and VI, the distribution coefficients and selectivities are reported. The distribution coefficient for component i is expressed as

$$K_i = \frac{x_i}{x_i'}$$

where x_i and x_i' are the mole fractions of the component in the heavy phase and light phase, respectively. The selectivity for component i in relation to component $\dot{\gamma}$ is expressed in the usual way as the ratio of the distribution coefficient for component i to that of component $\dot{\gamma}$:

$$S_{i\dot{\gamma}} = k_i/k_{\dot{\gamma}}$$

It is shown that the selectivities for toluene are less than 3 with most of the toluene appearing in the light phase. The selectivity in the ternary system of toluene, heptane, and benzyl alcohol is lower than that observed in the ternary system of toluene, heptane, and tri(ethylene glycol).

The quaternary system containing toluene, heptane, tri(ethylene glycol), and benzyl alcohol was treated as a pseudobinary system in order to obtain the UCST under the given mole fractions of hydrocarbon mixtures and solvent mixtures. Pseudocomponent 1 was the mixture of tri(ethylene glycol) and

Table VIII. Data for the Binodal and Phase Boundary Curve of Quaternary System (2): Pseudocomponent 1 Containing 8 mol % Tri(ethylene glycol) and 92 mol % Benzyl Alcohol and Pseudocomponent 2 Containing 25 mol % Toluene and 75 mol % Heptane

x_1	x_2	temp, °C	x_1	x_2	temp, °C
0.7936	0.2064	29.4	0.4492	0.5506	51.2
0.7718	0.2282	36.0	0.4083	0.5917	50.9
0.7324	0.2676	41.0	0.3103	0.6897	50.0
0.7322	0.2678	41.6	0.2730	0.7270	49.8
0.7280	0.2720	42.3	0.2658	0.7342	49.6
0.6712	0.3208	47.7	0.2478	0.7522	49.4
0.6691	0.3309	47.8	0.1932	0.8068	49.0
0.6505	0.3495	48.9	0.1607	0.8393	47.6
0.6197	0.3803	49.7	0.1392	0.8608	44.8
0.5801	0.4109	50.2	0.1239	0.8761	41.8
0.5351	0.4649	50.7	0.1080	0.8920	40.1
0.5093	0.4907	50.9	0.0940	0.9060	38.9
0.5078	0.4922	51.0	0.0851	0.9149	35.3

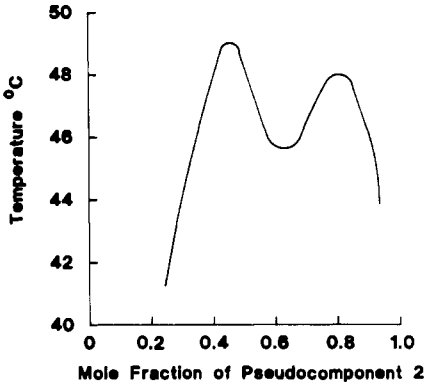

Figure 6. Binodal curve for quaternary system 1: pseudocomponent 1, 20 mol % tri(ethylene glycol) and 80 mol % benzyl alcohol; pseudocomponent 2, 50 mol % toluene and 50 mol % heptane.

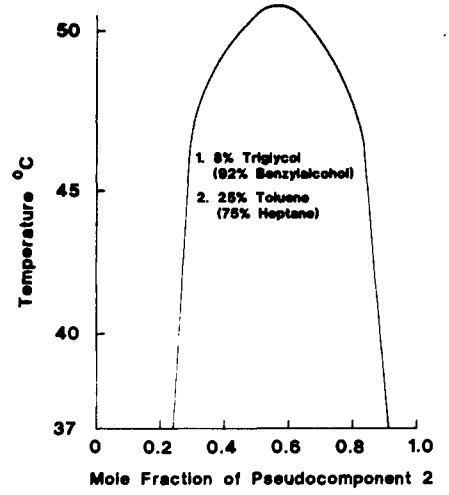

Figure 7. Binodal curve for quaternary system 2: pseudocomponent 1, 8 mol % tri(ethylene glycol) and 92 mol % benzyl alcohol; pseudocomponent 2, 25 mol % toluene and 75 mol % heptane.

Table IX. Data for the Binodal and Phase Boundary Curve of Quaternary System (3): Pseudocomponent 1 Containing 5 mol % Tri(ethylene glycol) and 95 mol % Benzyl Alcohol and Pseudocomponent 2 Containing 25 mol % Toluene and 75 mol % Heptane

x_1	x_2	temp, °C	x_1	x_2	temp, °C
0.7248	0.2752	34.1	0.4297	0.5703	38.5
0.6984	0.3016	35.9	0.3846	0.6154	37.8
0.6621	0.3379	38.9	0.2754	0.7246	36.1
0.5642	0.4358	40.0	0.2346	0.7654	34.2
0.5002	0.4998	39.7	0.1949	0.8051	32.8
0.4613	0.5387	39.0	0.1626	0.8374	31.0

benzyl alcohol, and pseudocomponent 2 was the mixture of the two hydrocarbons. The data for the binodal and phase boundary curves are given in Tables VII–IX, and the curves are shown in Figures 6–8.

The curve shown in Figure 6 has two maxima and is concave. The curves in Figures 7 and 9 are normal and have an UCST. This UCST is dependent on the compositions of both pseudocomponent 1 and pseudocomponent 2. The lower the content of toluene in the hydrocarbon mixture, the greater the content of tri(ethylene glycol) in the solvent mixture, then the higher is the UCST.

The liquid–liquid equilibrium data for the quaternary system are listed in Tables X and XI. The values of the distribution coefficient and selectivity are also included in those two tables. By comparison with the data shown in Table V, the selectivity increases with tri(ethylene glycol) is added to the benzyl alcohol. However, the selectivity decreases as the temperature rises.

In Table X are also listed the ratios of the solvent mixture to hydrocarbon mixture. The selectivity increases slightly as the ratio increases.

Discussion

Tri(ethylene glycol) has a good selectivity for toluene over heptane and other advantages, such as a high boiling point and

Table X. LLE Data for Quaternary Systems at 40 °C with Different Mixtures of Hydrocarbon and Solvent

Hydrocarbon Mixture Containing 25 mol % Toluene (1) and 75 mol % Heptane (2); Solvent Mixture Containing 8 mol % Tri(ethylene glycol) (3) and 92 mol % Benzyl Alcohol (4)

	heavy-phase mole fraction				light-phase mole fraction			
no.	x_1	x_2	x_3	x_4	x_1'	x_2'	x_3'	x_4'
1	0.1177	0.2244	0.0626	0.5953	0.1581	0.6047	0.0112	0.2260
2	0.1027	0.2010	0.0621	0.6342	0.1414	0.6473	0.0081	0.2032
3	0.0909	0.1986	0.0617	0.6487	0.1270	0.6662	0.0073	0.1995
4	0.0764	0.1907	0.0612	0.6717	0.1111	0.7021	0.0043	0.1825
5	0.0683	0.1805	0.0607	0.6905	0.1004	0.7173	0.0030	0.1793

			distribution coefficient		
no.	solvent/hydrocarbon	heavy phase/light phase	toluene	heptane	selectivity
1	0.7426	0.8169	0.7445	0.3711	2.01
2	1.2033	2.0083	0.7263	0.3105	2.34
3	1.4219	3.1376	0.7157	0.2981	2.40
4	2.0917	8.9300	0.6877	0.2716	2.53
5	2.4901	14.2022	0.6802	0.2512	2.71

Hydrocarbon Mixture Containing 20 mol % Toluene (1) and 80 mol % Heptane (2); Solvent Mixture Containing 8 mol % Tri(ethylene glycol) (3) and 92 mol % Benzyl Alcohol (4)

	heavy-phase mole fraction				light-phase mole fraction			
no.	x_1	x_2	x_3	x_4	x_1'	x_2'	x_3'	x_4'
1	0.0882	0.1901	0.0670	0.6548	0.1269	0.7017	0.0049	0.1655
2	0.0780	0.1894	0.0660	0.6666	0.1117	0.7206	0.0040	0.1637
3	0.0627	0.1793	0.0638	0.6942	0.0966	0.7457	0.0029	0.1548
4	0.0598	0.1745	0.0625	0.7032	0.0941	0.7725	0.0019	0.1315

			distribution coefficient		
no.	solvent/hydrocarbon	heavy phase/light phase	toluene	heptane	selectivity
1	0.7771	0.9379	0.6953	0.2705	2.57
2	0.2670	2.2994	0.6983	0.2628	2.66
3	1.7849	4.1591	0.6491	0.2404	2.70
4	2.1355	6.4625	0.6354	0.2259	2.81

Table XI. LLE Data for the Quaternary System Toluene (1), Heptane (2), Tri(ethylene glycol) (3), and Benzyl Alcohol (4) at 25 °C

	heavy-phase mole fraction				light-phase mole fraction			
no.	x_1	x_2	x_3	x_4	x_1'	x_2'	x_3'	x_4'
1	0.0650	0.1333	0.0648	0.7369	0.0948	0.8387	0.0004	0.0661
2	0.0752	0.1313	0.0688	0.7247	0.1156	0.8004	0.0006	0.0834
3	0.0851	0.1415	0.0741	0.6993	0.1323	0.7548	0.0008	0.1011
4	0.0895	0.1447	0.0752	0.6906	0.1423	0.7219	0.0011	0.1347
5	0.0299	0.1243	0.0720	0.7738	0.0494	0.8436	0.0019	0.1051
6	0.0314	0.1314	0.0725	0.7647	0.0566	0.8181	0.0029	0.1224
7	0.0353	0.1356	0.0736	0.7545	0.0591	0.7832	0.0047	0.1530

	distribution coefficient				distribution coefficient		
no.	toluene	heptane	selectivity	no.	toluene	heptane	selectivity
1	0.6857	0.1589	4.32	5	0.6053	0.1473	4.11
2	0.6505	0.1640	3.97	6	0.5548	0.1606	3.45
3	0.6432	0.1846	3.48	7	0.5973	0.1731	3.45
4	0.6290	0.2004	3.14				

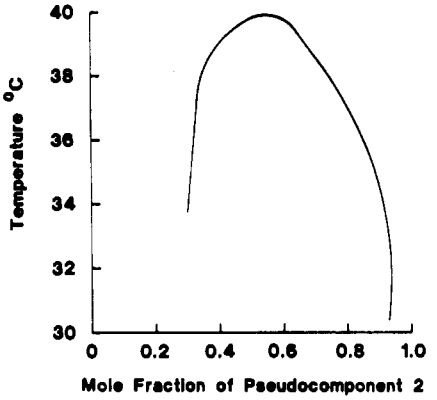

Figure 8. Binodal curve for quaternary system 3: pseudocomponent 1, 5 mol % tri(ethylene glycol) and 95 mol % benzyl alcohol; pseudocomponent 2, 25 mol % toluene and 75 mol % heptane.

density, so it is a good solvent for separation of toluene from the hydrocarbon mixture. However, it is not suitable for temperature-swing extraction.

The ternary system of benzyl alcohol, toluene, and heptane can be used in temperature-swing extraction, but the selectivity is lower and the content of toluene in the hydrocarbon mixture is less. A combination of benzyl alcohol and tri(ethylene glycol) may produce a better solvent mixture for the separation of toluene from the hydrocarbon mixture.

The present work gives the conditions for temperature-swing extraction. It is shown in Figures 6–8 that the system can be heated to 60 °C to produce a homogeneous phase and then it can be cooled to 40 °C to separate it into two phases. The waste heat from a refinery could be used for heating, and plant water is an appropriate cooling agent.

It will be necessary to improve the selectivity. A feasible approach is to increase the content of the tri(ethylene glycol) in the solvent mixture until the UCST of the system is raised to 80 °C . Another possibility is to decrease the temperature in the separation stage.

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