

Ternary Liquid–Liquid Equilibria for Pseudoternary Mixtures Containing an *n*-Alkane + an Aromatic Hydrocarbon + {*N*-Methyl-2-pyrrolidinone + a Solvent} at 298.2 K and 1 atm

Rolandra D. Naidoo, Trevor M. Letcher,* and Deresh Ramjugernath

School of Chemical Engineering, Thermodynamic Research Group, University of Natal, Durban 4041, South Africa

The binodal curves and liquid–liquid equilibrium data are presented for pseudoternary mixtures of *n*-hexane + toluene + (*N*-methyl-2-pyrrolidinone + a solvent). The solvents used in this investigation were glycerol, monoethylene glycol, diethylene glycol, triethylene glycol, and water. The results are discussed in terms of the separation selectivity of related systems, and the binodal curve data were fitted to the Hlavaty equation, the β -density function, and the logarithmic- γ function. The binodal curves showed good correlation with these equations. The NRTL and UNIQUAC equations were used to correlate the experimental tie-lines, which showed reasonable correlation.

Introduction

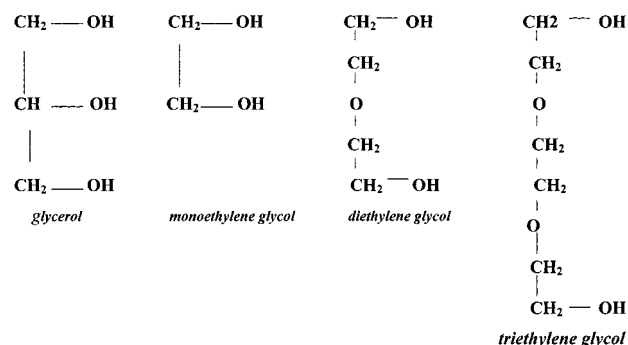
This study is part of an ongoing investigation to find an efficient solvent or solvent mixtures for extracting aromatic compounds from aliphatic compounds using solvent extraction. Liquid extraction is widely used in industry as a cheaper alternative or precursor to distillation, in the separation of aromatic and aliphatic compounds. Several commercial processes are available, including the widely used Arosolvan process.¹

In this work, liquid–liquid equilibrium related to the separation of an aromatic (toluene was used in this work) and an aliphatic (*n*-hexane was used here) using *N*-methyl-2-pyrrolidinone (NMP) and NMP mixed with glycerol, a glycol, or water. Mixed solvents of these types, as have previously been reported,^{2,3} are investigated. This work quantifies their separation, and the results can be used in the design of separation equipment. Although most of the systems in this work contain four components, the results have been represented as pseudoternary systems, as has been done previously.^{2,3,5–8}

In this work, the NMP mixed with a polyhydroxy compound, glycerol, (1,2,3-propanetriol), diethylene glycol (2,2'-oxybisethanol), or triethylene glycol (2,2'-[1,2-ethanediylbis(oxy)]bisethanol), was used to investigate the separation of toluene from *n*-hexane. These results were compared to those obtained using the mixed solvents {NMP + monoethylene glycol} or {NMP + water}, the solvents that form the basis of the Arosolvan process.

The three polyhydroxy compounds, glycerol, diethylene glycol, and triethylene glycol, were chosen because of their similarity to monoethylene glycol, which proved to be so

effective in the Arosolvan process (the structures of the relevant compounds are given below)



Data for the mixtures studied were determined at 298 K and 1 atm. The results are discussed in terms of the extent of the two-phase region and the selectivity, *S*, of the solvent as defined by Letcher and Deenadayalu.⁹

The binodal curves were correlated using the Hlavaty equations,¹⁰ the β -density function, and the logarithmic- γ function.¹¹

The NRTL¹² and UNIQUAC¹³ equations were used for correlating the experimental tie-lines for the various systems.

Experimental Section

Chemicals. Toluene had a purity greater than 99 mol % and was stored under 4A molecular sieves. The solvent *N*-methyl-2-pyrrolidinone had a purity greater than 98 mol % and was not purified further due to the fact that it is an

* To whom correspondence should be addressed. E-mail: Letcher@nu.ac.za.

expensive chemical and distillation would have proved too costly, due to the loss of significant amounts of the chemical for a very small increase in purity. The *n*-hexane had a purity of greater than 99 mol % and was used without further purification. The glycols used in the investigation had purities greater than 97 mol % and were also used without further treatment. The presence of the impurities did not significantly affect the experimental work.

Procedure. The binodal curves were determined using the cloud point titration technique as described by Letcher and Siswana.¹⁴ The accuracy of this technique was greater than 0.005 mass fraction. Tie-lines were determined using the refractive index method described by Briggs and Comings.¹⁵ The precision of the technique used to determine the tie-lines was better than 0.01 mass fraction. Plait-points were determined using the method outlined by Treybal.¹⁶

Results

The compositions of mixtures (mass fractions) on the binodal curves at 298.2 K are given in Table 1. The compositions of the conjugate phases are given in Table 2. The compositions of the plait-points are given in Table 3. The maximum selectivity for each solvent is given in Table 4. The binodal curves and tie-line results have been plotted in Figure 1. Three equations have been used to correlate the binodal curve data following the work of Hlavaty.¹⁰

The coefficients A_i relate to the modified Hlavaty equation

$$x_2 = A_1 x_A \ln x_A + A_2 x_B \ln x_B + A_3 x_A x_B \quad (1)$$

The coefficients B_i relate to the β function equation:

$$x_2 = B_1(1 - x_A)B_2x_3B_3 \quad (2)$$

and the coefficients C_i relate to the log- γ equation:

$$x_2 = C_1(-\ln x_A)C_2x_A C_3 \quad (3)$$

where

$$x_A = \frac{x_1 + 0.5x_2 - x_1^\circ}{x_{11}^\circ - x_1^\circ} \quad (4)$$

$$x_B = \frac{x_{11}^\circ - x_1 - 0.5x_2}{x_{11}^\circ - x_1^\circ} \quad (5)$$

and x_1 refers to the mole fraction of the *n*-hexane and x_2 refers to the mole fraction of the toluene. x_{11}° and x_1° refer to the values of x_1 which cut the binodal curve at the $x_2 = 0$ axis.

The coefficients A_i , B_i , and C_i along with the error β , the error γ , and the standard deviation are given in Table 5.

The standard deviation is defined as follows:

$$\sigma = \left[\frac{\sum \{x_{2\text{calc}} - x_{2\text{exp}}\}^2}{n - 3} \right]^{0.5} \quad (6)$$

where n is the number of data points and 3 is the number of coefficients.

Table 1. Binodal Curve Compositions at 298 K and 1 atm for the Mixtures $\{\omega_1(n\text{-hexane}) + \omega_2(\text{toluene}) + (1 - \omega_1 - \omega_2)[\text{NMP} + \text{a Solvent}]\}$

ω_1	ω_2	ω_1	ω_2
NMP		NMP + 10 mass % Glycerol	
0.909	0.000	0.959	0.000
0.817	0.084	0.806	0.175
0.802	0.063	0.723	0.260
0.753	0.113	0.647	0.338
0.632	0.165	0.562	0.424
0.601	0.149	0.424	0.553
0.389	0.185	0.370	0.603
0.203	0.105	0.230	0.701
0.155	0.000	0.102	0.117
		0.096	0.062
		0.089	0.332
		0.088	0.000
NMP + 30 mass % Glycerol		NMP + 10 mass % Monoethylene Glycol	
0.980	0.000	0.983	0.000
0.762	0.197	0.877	0.097
0.628	0.319	0.643	0.314
0.494	0.455	0.622	0.318
0.455	0.468	0.567	0.361
0.130	0.670	0.401	0.441
0.024	0.475	0.364	0.444
0.021	0.326	0.335	0.429
0.020	0.409	0.128	0.228
0.008	0.000	0.095	0.000
NMP + 30 mass % Monoethylene Glycol		NMP + 10 mass % Diethylene Glycol	
0.983	0.000	0.990	0.000
0.765	0.183	0.854	0.123
0.591	0.379	0.600	0.376
0.475	0.481	0.461	0.447
0.278	0.706	0.439	0.464
0.227	0.764	0.436	0.468
0.019	0.811	0.288	0.411
0.074	0.270	0.207	0.245
0.066	0.171	0.185	0.221
0.085	0.000	0.086	0.000
NMPI + 10 mass % Triethylene Glycol		NMP + 10 mass % Water	
0.991	0.000	0.982	0.000
0.894	0.089	0.950	0.040
0.703	0.277	0.939	0.045
0.590	0.335	0.852	0.133
0.478	0.314	0.603	0.386
0.366	0.251	0.489	0.490
0.139	0.095	0.449	0.550
0.080	0.059	0.204	0.771
0.072	0.000	0.120	0.875
		0.020	0.971
		0.034	0.171
		0.029	0.107
		0.021	0.032
		0.012	0.000
		0.010	0.981
		0.000	0.568

Data on the binodal curves have all been represented in terms of the mass fractions, and the conversion from mass to mole fractions have been performed using the following equation:

$$x_i = \frac{\omega_i M_j M_k}{\omega_i M_j M_k + \omega_j M_i M_k + \omega_k M_i M_j} \quad (7)$$

where x_i refers to the mole fraction of species i and ω_i refers to the mass fraction of species i . M_i refers to the molecular weight of species i .

Discussion

The effectiveness of extracting the aromatic compound by the solvent concerned is given by its selectivity (S),

Table 2. Compositions of Conjugate Solutions (ω_1 , ω_2 , ω_1'' , ω_2'') for $\{\omega_1(n\text{-Hexane}) + \omega_2(\text{Toluene}) + (1 - \omega_1 - \omega_2)(\text{NMP} + \text{a Solvent})\}$ at 298 K and 1 atm

ω_1'	ω_2'	ω_1''	ω_2''
		NMP	
0.866	0.035	0.172	0.056
0.800	0.082	0.176	0.087
0.714	0.126	0.221	0.126
0.643	0.156	0.276	0.156
		NMP + 10 mass % Glycerol	
0.400	0.578	0.101	0.040
0.356	0.613	0.097	0.098
0.322	0.642	0.133	0.115
0.225	0.694	0.090	0.272
		NMP + 30 mass % Glycerol	
0.871	0.077	0.017	0.052
0.816	0.137	0.020	0.073
0.684	0.266	0.020	0.121
0.500	0.440	0.020	0.226
0.400	0.534	0.020	0.298
0.286	0.617	0.020	0.387
		NMP + 10 mass % Monoethylene Glycol	
0.939	0.038	0.095	0.023
0.815	0.163	0.095	0.023
0.686	0.273	0.095	0.023
0.499	0.402	0.095	0.023
0.296	0.439	0.095	0.023
		NMP + 30 mass % Monoethylene Glycol	
0.732	0.213	0.099	0.076
0.509	0.461	0.094	0.106
0.394	0.587	0.080	0.188
0.253	0.726	0.057	0.298
0.159	0.800	0.032	0.441
		NMP + 10 mass % Diethylene Glycol	
0.699	0.294	0.100	0.029
0.657	0.337	0.110	0.048
0.464	0.448	0.118	0.063
0.386	0.452	0.194	0.250
		NMP + 10 mass % Triethylene Glycol	
0.918	0.077	0.079	0.041
0.842	0.150	0.079	0.041
0.772	0.224	0.079	0.041
0.699	0.280	0.079	0.041
0.598	0.325	0.079	0.041
		NMP + 10 mass % Water	
0.617	0.369	0.017	0.037
0.593	0.395	0.028	0.088
0.564	0.420	0.031	0.219
0.545	0.442	0.023	0.322
0.472	0.512	0.017	0.439

Table 3. Compositions of Plait-Points for the Mixtures $\{\omega_1(n\text{-Hexane}) + \omega_2(\text{Toluene}) + (1 - \omega_1 - \omega_2)(\text{NMP} + \text{a Solvent})\}$ at 298 K and 1 atm

	ω_1	ω_2
pure NMP	0.551	0.173
10 mass % glycerol	0.090	0.382
30 mass % glycerol	0.032	0.540
10 mass % monoethylene glycol	0.112	0.121
30 mass % monoethylene glycol	0.009	0.661
10 mass % diethylene glycol	0.301	0.419
10 mass % triethylene glycol	0.079	0.041
10 mass % water	0.061	0.925

which is the measure of the ability of the solvent to separate the aromatic from the alkane:

$$S = \frac{\left(\frac{x_2}{x_1}\right)_{\text{solvent-rich phase}}}{\left(\frac{x_2}{x_1}\right)_{\text{alkane-rich phase}}} \quad (8)$$

Table 4. Maximum Selectivity Values for the Mixtures $\{\omega_1(n\text{-Hexane}) + \omega_2(\text{Toluene}) + (1 - \omega_1 - \omega_2)(\text{NMP} + \text{a Solvent})\}$ at 298 K and 1 atm

	S
pure NMP	6
10 mass % glycerol	558
30 mass % glycerol	38
10 mass % monoethylene glycol	290
30 mass % monoethylene glycol	118
10 mass % diethylene glycol	1224
10 mass % triethylene glycol	1078
10 mass % water	679

The two-phase region for the system containing only NMP as a solvent (see Figure 1a) is relatively small, indicating a small range of separation compositions. This system is henceforth referred to as the "base" system. The maximum selectivity obtained for this system was found to be almost 6.

The system containing NMP + 10 mass % glycerol (Figure 1b) showed a large increase in the two-phase region compared to the base system. As a result, the concentration range over which separation can be affected is significantly increased. Our results are similar to those obtained by Letcher and Naicker.¹⁷ The selectivity observed for this system was greater than 560, an increase of almost a 100-fold compared to our base system. On increasing the amount of glycerol added to the NMP to 30 mass % glycerol (Figure 1c), the binodal curve showed a very slight increase in the two-phase region; however, there seemed to be a very large decrease in the selectivity of the solvent to just below 38. A compromise has to be made between the range of separation and the selectivity of the solvent.

The system involving NMP + 10 mass % monoethylene glycol (Figure 1d) showed an increase in the two-phase region, as well as the selectivity compared to the base system. The maximum selectivity of the system containing 10 mass % monoethylene glycol was found to be about 280. The further addition of monoethylene glycol to NMP to a 30 mass % monoethylene glycol solution showed a remarkable increase in the area of the two-phase region (Figure 1e), larger than that found for the system containing NMP + 10 mass % monoethylene glycol, and also larger than those for all systems containing NMP + glycerol reported here. However, the selectivity of the solvent decreased to about 119.

These are still considerably less than the selectivity observed using NMP + 10 mass % glycerol. The solvent NMP + monoethylene glycol has been documented previously.¹⁹

The system containing a NMP + 10 mass % diethylene glycol solvent showed a slightly smaller increase in the area of the two-phase region (Figure 1f) compared to the systems mentioned above. The maximum selectivity however shows a phenomenal increase to a maximum selectivity of around 1200. The binodal curve also appears to be skewed toward the alkane-rich area of the curve.

The system containing NMP + 10 mass % triethylene glycol showed an even smaller increase in the two-phase region (Figure 1g) compared to the NMP + 10 mass % diethylene glycol system and showed a greater skewing toward the alkane-rich region. The selectivity of this solvent also showed a remarkable increase compared to the base system. The maximum selectivity obtained was nearly 1100.

With NMP + 10 mass % water the two-phase region (Figure 1h) appears to be the largest thus far encountered

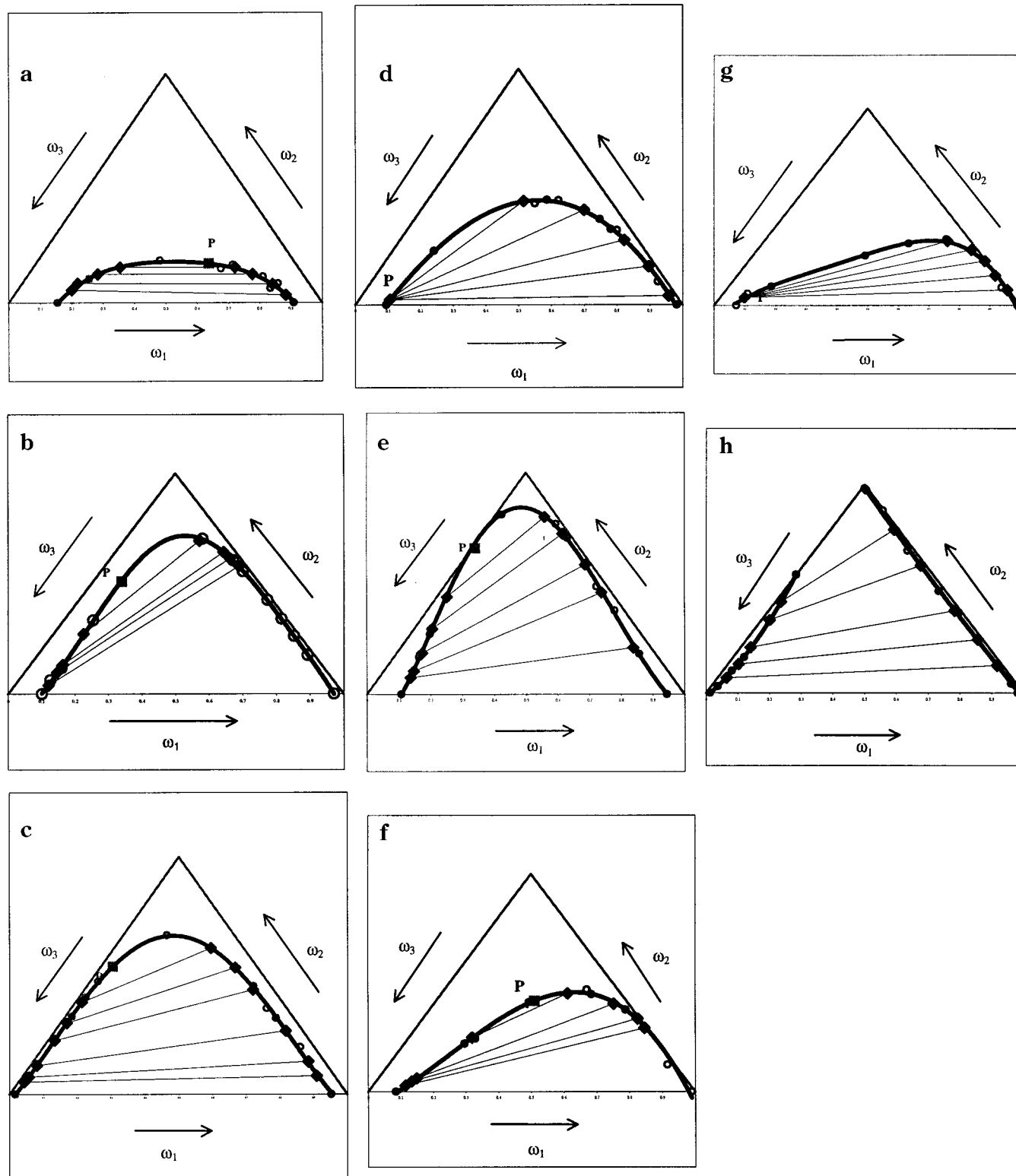


Figure 1. (a) Binodal curve for $\omega_1(\text{C}_6\text{H}_{14}) + \omega_2(\text{C}_6\text{H}_5\text{CH}_3) + \omega_3(\text{C}_5\text{H}_9\text{NO})$ at 298 K and 1 atm. (b) Binodal curve for $\omega_1(\text{C}_6\text{H}_{14}) + \omega_2(\text{C}_6\text{H}_5\text{CH}_3) + \omega_3(\text{C}_5\text{H}_9\text{NO} + 10 \text{ mass } \% \text{ CH}_2\text{OHCHOHCH}_2\text{OH})$ at 298 K and 1 atm. (c) Binodal curve for $\omega_1(\text{C}_6\text{H}_{14}) + \omega_2(\text{C}_6\text{H}_5\text{CH}_3) + \omega_3(\text{C}_5\text{H}_9\text{NO} + 30 \text{ mass } \% \text{ CH}_2\text{OHCHOHCH}_2\text{OH})$ at 298 K and 1 atm. (d) Binodal curve for $\omega_1(\text{C}_6\text{H}_{14}) + \omega_2(\text{C}_6\text{H}_5\text{CH}_3) + \omega_3(\text{C}_5\text{H}_9\text{NO} + 10 \text{ mass } \% (\text{CH}_2\text{OH})_2)$ at 298 K and 1 atm. (e) Binodal curve for $\omega_1(\text{C}_6\text{H}_{14}) + \omega_2(\text{C}_6\text{H}_5\text{CH}_3) + \omega_3(\text{C}_5\text{H}_9\text{NO} + 30 \text{ mass } \% (\text{CH}_2\text{OH})_2)$ at 298 K and 1 atm. (f) Binodal curve for $\omega_1(\text{C}_6\text{H}_{14}) + \omega_2(\text{C}_6\text{H}_5\text{CH}_3) + \omega_3(\text{C}_5\text{H}_9\text{NO} + 10 \text{ mass } \% \text{ HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})$ at 298 K and 1 atm. (g) Binodal curve of $\omega_1(\text{C}_6\text{H}_{14}) + \omega_2(\text{C}_6\text{H}_5\text{CH}_3) + \omega_3(\text{C}_5\text{H}_9\text{NO} + 10 \text{ mass } \% \text{ HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})$ at 298 K and 1 atm. (h) Binodal curve of $\omega_1(\text{C}_6\text{H}_{14}) + \omega_2(\text{C}_6\text{H}_5\text{CH}_3) + \omega_3(\text{C}_5\text{H}_9\text{NO} + 10 \text{ mass } \% \text{ H}_2\text{O})$ at 298 K and 1 atm.

and hence the largest range over which separation can occur. The selectivity however was close to 100.

The order of the size of the two-phase region is as follows: 10 mass % of water > 30 mass % monoethylene glycol > 30 mass % glycerol > 10 mass %

monoethylene glycol > 10 mass % diethylene glycol > 10 mass % triethylene glycol > pure NMP.

The solvents in decreasing order of selectivity are as follows: 10 mass % diethylene glycol > 10 mass % triethylene glycol > 10 mass % glycerol > 10 mass % monoeth-

Table 5. Hlavaty β , γ , and Error Values for $\{\omega_1(n\text{-Hexane}), \omega_2(\text{Toluene}), \text{and } (1 - \omega_1 - \omega_2)(\text{NMP} + \text{a Solvent})\}$ at 298 K and 1 atm

Pure NMP		
$A_1 = -0.515$	$B_1 = 0.315$	$C_1 = 0.295$
$A_2 = -0.529$	$B_2 = 0.454$	$C_2 = 0.43$
$A_3 = -0.786$	$B_3 = 0.51$	$C_3 = 0.646$
error(Hlavaty) = 0.011	error(β) = 0.01	error(γ) = 0.009
NMP + 10% Glycerol		
$A_1 = 1.045$	$B_1 = 3.496$	$C_1 = 3.083$
$A_2 = 0.604$	$B_2 = 1.137$	$C_2 = 1.086$
$A_3 = 4.993$	$B_3 = 1.297$	$C_3 = 1.677$
error(Hlavaty) = 0.013	error(β) = 0.015	error(γ) = 0.016
NMP + 30% Glycerol		
$A_1 = 1.031$	$B_1 = 4.298$	$C_1 = 3.917$
$A_2 = 1.295$	$B_2 = 1.402$	$C_2 = 1.364$
$A_3 = 5.826$	$B_3 = 1.333$	$C_3 = 1.875$
error(Hlavaty) = 0.012	error(β) = 0.011	error(γ) = 0.01
NMP + 10% MEG		
$A_1 = 0.201$	$B_1 = 2.133$	$C_1 = 2.001$
$A_2 = -0.009$	$B_2 = 1.088$	$C_2 = 1.065$
$A_3 = 2.046$	$B_3 = 1.142$	$C_3 = 1.564$
error(Hlavaty) = 0.008	error(β) = 0.01	error(γ) = 0.011
NMP + 30% MEG		
$A_1 = 1.512$	$B_1 = 8.362$	$C_1 = 6.963$
$A_2 = 2.746$	$B_2 = 1.836$	$C_2 = 1.754$
$A_3 = 9.12$	$B_3 = 1.531$	$C_3 = 2.172$
error(Hlavaty) = 0.022	error(β) = 0.014	error(γ) = 0.013
NMP + 10% DEG		
$A_1 = 1.536$	$B_1 = 3.929$	$C_1 = 3.68$
$A_2 = 0.323$	$B_2 = 1.313$	$C_2 = 1.29$
$A_3 = 4.42$	$B_3 = 1.772$	$C_3 = 2.302$
error(Hlavaty) = 0.013	error(β) = 0.011	error(γ) = 0.012
NMP + 10% TEG		
$A_1 = -0.027$	$B_1 = 0.974$	$C_1 = 0.883$
$A_2 = -0.941$	$B_2 = 0.74$	$C_2 = 0.7$
$A_3 = -0.172$	$B_3 = 0.929$	$C_3 = 1.166$
error(Hlavaty) = 0.023	error(β) = 0.032	error(γ) = 0.033
NMP + 10% Water		
$A_1 = 1.926$	$B_1 = 4.145$	$C_1 = 3.724$
$A_2 = 2.04$	$B_2 = 1.134$	$C_2 = 1.105$
$A_3 = 8.996$	$B_3 = 1.328$	$C_3 = 1.714$
error(Hlavaty) = 0.05	error(β) = 0.078	error(γ) = 0.075

Table 6. Physical Properties of the Pure Components at 298 K

	$V_m^b/(\text{cm}^3 \cdot \text{mol}^{-1})$	surface parameters ^a	
		Q	R
NMP	96.63	3.228	3.91778
glycerol	73.37	2.508	4.7957
monoethylene glycol	55.92	3.48	3.3488
diethylene glycol	95.36	4.8	4.94159
triethylene glycol	134.14	6.12	6.53429
water	18.07	1.4	0.92
hexane	131.60	3.856	4.4998
toluene	107.18	2.968	3.3228

^a Reference 21. ^b Reference 20.

ylene glycol > 30 mass % monoethylene glycol > 10 mass % water > 30 mass % glycerol > pure NMP.

The fitting of the Hlavaty equation,¹⁰ the β -density function, and the logarithmic- γ function¹¹ to our bimodal curves showed good correlation. The nonrandom two-liquid equation (NRTL)¹² and the universal quasichemical equation (UNIQUAC)¹³ were used to correlate the experimental tie-lines for the eight ternary mixtures reported. The equations used follow the algorithm proposed by Walas.¹⁹ The values for the surface parameters, Q and R , along with the molar volumes, V_m , are given in Table 6. The objective function, $F(P)$, used to minimize the difference between the experimental and calculated concentrations is defined as

Table 7. Values of the Parameters for the NRTL and UNIQUAC Equations as Well as the Root Mean Squared Deviation (rmsd) Values

component	NRTL			UNIQUAC			
	$i-j$	$g_{ij} - g_{ji}$ J·mol ⁻¹	rmsd	$g_{ij} - g_{ji}$ J·mol ⁻¹	Δu_{ij} J·mol ⁻¹	rmsd	Δu_{ij} J·mol ⁻¹
NMP							
0.0577							
1-2	2-1	-346.69		1333.48	0.0086		0.1866
1-3	3-1	3060.87		3771.62	-0.1475		0.1483
2-3	3-2	-5789.61		-2472.67	0.079		0.2155
NMP + 10% (w/w) Glycerol							
0.1268							
1-2	2-1	-4237.7		-1803.24	0.1273		-0.14273
1-3	3-1	-249.01		966.86	-0.0134		-0.000056
2-3	3-2	2225.38		2798.74	0.03207		0.07249
NMP + 30% (w/w) Glycerol							
0.088							
1-2	2-1	-4826.23		-1700.65	-3649.11		-2053.73
1-3	3-1	3382.68		7194.03	-355.1		1749.21
2-3	3-2	1742.77		400.82	2230.03		2080.78
NMP + 10% (w/w) MEG							
0.1546							
1-2	2-1	-182.73		1792.79	0.01503		-0.03615
1-3	3-1	2396.46		1757.24	0.07688		0.0077
2-3	3-2	111.75		-3916.02	-0.2814		0.06268
NMP + 30% (w/w) MEG							
0.096							
1-2	2-1	-4066.47		-784.52	0.0792		0.004889
1-3	3-1	2873.56		1720.56	0.004397		0.0044
2-3	3-2	1962.9		1474.82	0.004536		0.009412
NMP + 10% (w/w) DEG							
0.0666							
1-2	2-1	-9799.32		-540.31	0.05717		0.00722
1-3	3-1	3221.24		4335.13	0.04642		0.05012
2-3	3-2	3632.67		-1626.28	-0.02024		0.00085
NMP + 10% (w/w) TEG							
0.0418							
1-2	2-1	-3315.88		-7291.06	0.0262		0.03477
1-3	3-1	6151.53		3101.04	-0.04909		-0.08737
2-3	3-2	3609.39		-2515.94	0.05356		0.09509
NMP + 10% (w/w) Water							
0.148							
1-2	2-1	-1637.79		-2378.53	-0.1677		-0.01739
1-3	3-1	2817.35		2478.74	0.07648		0.07588
2-3	3-2	-1726.38		523.09	0.01419		0.04635

$$F(P) = \sum_{i=1}^n [x_{1i}' - x_{1i}'(\text{calc})(PT)]^2 + [x_{2i}' - x_{2i}'(\text{calc})(PT)]^2 + [x_{1i}'' - x_{1i}''(\text{calc})]^2 + [x_{2i}'' - x_{2i}''(\text{calc})(PT)]^2 \quad (9)$$

where P is the set of parameters vector, n is the number of experimental points, $x_{1i}'(\text{exp})$, $x_{2i}'(\text{exp})$ and $x_{1i}'(\text{calc})$, $x_{2i}'(\text{calc})$ are the experimental and calculated mole fractions of one phase and $x_{1i}''(\text{exp})$, $x_{2i}''(\text{exp})$ and $x_{1i}''(\text{calc})$, $x_{2i}''(\text{calc})$ are the experimental and calculated mole fractions of the other phase. For the NRTL model the nonrandomness parameter, α_{ij} , was set at 0.30 (see Table 7). The NRTL equation was optimized for all parameters. The model parameters for the NRTL and UNIQUAC equations are shown in the table together with the root-mean-squared deviation (rmsd) values, defined below. This may be regarded as a measure of the precision of the correlation:

$$\text{rmsd} = \left\{ \frac{\sum_i \sum_l \sum_m [x_{ilm}^{\text{exp}} - x_{ilm}^{\text{calc}}]^2}{6k} \right\}^{1/2} \quad (10)$$

where x is the mole fraction and the subscripts i , l , and m designate the component, phase, and tie-line, respectively,

and k designates the number of interaction components. The correlation obtained showed similar results for both the NRTL and UNIQUAC models.

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