Mutual Solubility and Lower Critical Solution Temperature for Water + Glycol Ether Systems

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Mutual solubility and the lower critical solution temperature (LCST) are reported for a number of water + ethylene glycol ether and water + propylene glycol ether systems near atmospheric pressure. For the systems studied, the LCST is in the range of −10 °C to 48 °C. Glycol ethers are unusual organic solvents in that they have both hydrophobic and hydrophilic functionality and can hydrogen bond with water. Because of this, their interactions with water are complex and difficult to predict. The presence of an LCST is characteristic of hydrogen-bonding mixtures, and the value of the LCST reflects the relative magnitude of hydrophobic/hydrophilic interactions in solution. A higher LCST value is indicative of a glycol ether with greater hydrophilic character. For water + ethylene glycol ether mixtures, the glycol ether becomes increasingly hydrophilic (LCST increases) as the number of oxyalkylene repeating units increases. The opposite effect is seen for water + propylene glycol ether mixtures. In this case, the glycol ether becomes more hydrophobic (LCST decreases) as the number of oxyalkylene repeating units increases. The results clearly demonstrate that water + glycol ether interactions are strong functions of both chemical structure and temperature.

Introduction

Glycol ethers are oxygenated hydrocarbons containing a primary or secondary hydroxyl group at one end, an alkyl ether linkage at the other, and a total of up to three oxyalkylene repeating units in the middle (typically oxyethylene $O-CH_2CH_2-$ or oxypropylene $-O-CH(CH_3)-CH_2-$). Compounds with more than three oxyalkylene repeating units normally are called polyglycols. Most commercially available glycol ethers are derived from the acid- or base-catalyzed reaction of an aliphatic alcohol or phenol with ethylene oxide (EO) or propylene oxide (PO). The resulting compounds are commonly known as mono-, di-, and triethylene glycol ethers or mono-, di-, and tripropylene glycol ethers.

Glycol ethers are used commercially in a wide range of product formulations and industrial process applications. They are used as solvents in cleaning solutions, paints, coatings, and inks. Glycol ethers are useful cosolvents and are utilized in both organic-based and water-based formulations. They also find use as special-purpose fluids including automotive brake fluids and industrial process solvents. Many glycol ethers are biodegradable and exhibit low aquatic and mammalian toxicity.[1−5] For these reasons, they have garnered increasing interest as relatively benign alternatives to certain conventional solvents. Over 1 million metric tons of glycol ethers were consumed in 1999 in the regions of North America, Western Europe, Japan, and Brazil.[6]

This paper reports mutual solubility data for liquid−liquid equilibrium for a number of water + ethylene glycol ether and water + propylene glycol ether mixtures. Because glycol ethers can hydrogen bond with water (participating in both proton donor and proton acceptor interactions) and because they possess both hydrophobic as well as hydrophilic functional groups, their behavior in water is complex and difficult to predict. Unlike most organic solvents, glycol ethers exhibit so-called inverse solubility in water. That is, within the range of normal process temperatures, many water + glycol ether systems exhibit a lower critical solution temperature (LCST) below which the system is completely miscible in all proportions. Above the LCST, partial liquid miscibility occurs and the solubility of the glycol ether in water decreases with increasing temperature. This inverse solubility behavior can be attributed to temperature-sensitive hydrogen bonding. At temperatures below the LCST, the glycol ether is able to form hydrogen bonds with water and this attractive interaction leads to complete miscibility. Above the LCST, the ability of the glycol ether to hydrogen bond with water is reduced because of increasing thermal (kinetic) energy. As a result, hydrophobic interactions begin to dominate as temperature increases. Solvent systems that exhibit this LCST behavior have been suggested for applications where the ability to switch between a two-liquid-phase system and a single-liquid-phase system by changing temperature offers advantages. These include use in novel cleaning and extraction processes[7−9] and for catalyst recovery from homogeneous reaction mixtures.[10] The data reported here supplement existing literature data and may be helpful in improving methods used to predict phase equilibrium or in developing new uses of glycol ethers.

Experiments

Materials. The materials used in this study include water, 11 ethylene glycol ethers, and 6 propylene glycol ethers. The 11 ethylene glycol ethers are ethylene glycol *n*-butyl ether, ethylene glycol *n*-pentyl ether, diethylene glycol *n*-pentyl ether, ethylene glycol 2-methyl-1-butyl

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Table 1. Description, Source, and Purity of Materials

compound	structure	source	purity/%
water	HOH	in-house	distilled
acetone	CH_3COCH_3	Baker	99.9
tetrahydrofuran	$(CH_2)_4O$	Fisher	99.9
toluene	$C_6H_5CH_3$	Baker	99.9
ethylbenzene	$C_6H_5CH_2CH_3$	Aldrich	99
ethylene glycol methyl ether	$CH_3OCH_2CH_2OH$	Aldrich	99.9
diethylene glycol *n*-butyl ether	$CH_3(CH_2)_3(OCH_2CH_2)_2OH$	Fisher	99
	Ethylene Glycol Ethers		
ethylene glycol *n*-butyl ether	$CH_3(CH_2)_3OCH_2CH_2OH$	Aldrich	99.5
ethylene glycol *n*-pentyl ether	$CH_3(CH_2)_4OCH_2CH_2OH$	Dow	99.6
diethylene glycol *n*-pentyl ether	$CH_3(CH_2)_4(OCH_2CH_2)_2OH$	Dow	97
ethylene glycol 2-methyl-1-butyl ether	$CH_3CH_2CH(CH_3)CH_2OCH_2CH_2OH$	Dow	99
diethylene glycol 2-methyl-1-butyl ether	$CH_3CH_2CH(CH_3)CH_2(OCH_2CH_2)_2OH$	Dow	99
ethylene glycol *n*-hexyl ether	$CH_3(CH_2)_5OCH_2CH_2OH$	Dow	99
diethylene glycol *n*-hexyl ether	$CH_3(CH_2)_5(OCH_2CH_2)_2OH$	Dow	97
triethylene glycol *n*-hexyl ether	$CH_3(CH_2)_5(OCH_2CH_2)_3OH$	Dow	96.6
ethylene glycol *n*-heptyl ether	$CH_3(CH_2)_6OCH_2CH_2OH$	Dow	99.3
diethylene glycol *n*-heptyl ether	$CH_3(CH_2)_6(OCH_2CH_2)_2OH$	Dow	99.7
triethylene glycol *n*-heptyl ether	$CH_3(CH_2)_6(OCH_2CH_2)_3OH$	Dow	99
	Propylene Glycol Ethers		
propylene glycol *n*-propyl ether	$CH_3(CH_2)_2OCH_2CH(CH_3)OH$	Dow	99.0+
dipropylene glycol *n*-propyl ether	$CH_3(CH_2)_2[OCH_2CH(CH_3)]_2OH$	Dow	98.5+
tripropylene glycol *n*-propyl ether	$CH_3(CH_2)_2[OCH_2CH(CH_3)]_3OH$	Dow	95.0+
propylene glycol *n*-butyl ether	$CH_3(CH_2)_3OCH_2CH(CH_3)OH$	Dow	99.0+
dipropylene glycol *n*-butyl ether	$CH_3(CH_2)_3[OCH_2CH(CH_3)]_2OH$	Dow	98.5+
tripropylene glycol *n*-butyl ether	$CH_3(CH_2)_3[OCH_2CH(CH_3)]_3OH$	Dow	95.0+

ether, diethylene glycol 2-methyl-1-butyl ether, ethylene glycol *n*-hexyl ether, diethylene glycol *n*-hexyl ether, triethylene glycol *n*-hexyl ether, ethylene glycol *n*-heptyl ether, diethylene glycol *n*-heptyl ether, and triethylene glycol *n*-heptyl ether. The six propylene glycol ethers are propylene glycol *n*-propyl ether, dipropylene glycol *n*-propyl ether, tripropylene glycol *n*-propyl ether, propylene glycol *n*-butyl ether, dipropylene glycol *n*-butyl ether, and tripropylene glycol *n*-butyl ether. All of the propylene glycol ethers are mixtures of isomers but were treated as pure components in this work. Acetone, tetrahydrofuran, toluene, ethylbenzene, ethylene glycol methyl ether, and diethylene glycol *n*-butyl ether were also used as solvents. Table 1 presents the structure, source, and purity of each compound; for the propylene glycol ethers, the predominant isomer is shown. The purity of each of the glycol ethers used in the mutual solubility study was determined by the gas chromatographic methods described below, and, for the propylene glycol ethers, represents the sum of all isomers. Individual isomer compositions were not determined.

Experimental Equipment and Procedures. Equilibrium phases were sampled and analyzed for composition to determine mutual solubility. Separate equipment and procedures were used for water + ethylene glycol ether systems and water + propylene glycol ether systems because of individual laboratory preferences.

Water + Ethylene Glycol Ether Systems. The liquid−liquid equilibrium was achieved in a 0.5 l glass vessel in a constant-temperature bath. Water and the desired glycol ether were added to this vessel through 0.16 cm lines. The mixture was then stirred vigorously by a magnetic stirrer at the desired bath temperature. Stirring produced very fine droplets of each phase entrained in the other phase, which slowly separated after the liquid was still. Some systems required 24 h for the two phases to completely disengage. The temperature of the mixture in the vessel was measured by a calibrated platinum resistance thermometer with an uncertainty of ±0.05 °C. For all but two water + ethylene glycol ether systems, the pressure was kept slightly above atmospheric (~1.15 bar) to facilitate sample removal; for the water + ethylene glycol *n*-butyl ether and water + triethylene glycol *n*-hexyl ether systems, the pressure was maintained at the vapor pressure of the mixture.

After the liquid phases had separated, a large purge and three samples were withdrawn from each liquid phase into weighed glass vials. Samples were between (4 and 20) g, depending on the concentration of the minor component in the sample. Several methods were developed to analyze the samples based on the concentration of the minor component in the major component.

For aqueous samples where the minor component was fairly soluble in water, a solvent (acetone, ethylene glycol methyl ether, or diethylene glycol *n*-butyl ether) was added to the sample to keep all the compounds in one liquid phase and to serve as an internal standard. Then, an aliquot of each sample was analyzed for organic content by gas chromatography. Each aliquot was analyzed five times. The gas chromatographic analyses were performed by an HP-5890A gas chromatograph equipped with a DB-1 capillary column. The column was 30 m long with an internal diameter of 0.32 mm and a film thickness of 3 μm. Details of the gas chromatographic method are given in Table 2. Response factors were determined by analyzing gravimetrically prepared standards before each set of samples. Repeatability of the composition determination within each sample or standard was usually better than 1% of the measured value.

For an aqueous phase where the composition of the glycol ether was less than 30 mass %, the composition of water was found by difference. For an aqueous phase composed of more than 30 mass % glycol ether, samples were also withdrawn into three weighed syringes for analysis by Karl Fisher titration. The contents of each syringe were washed into the titrator vessel by using a long needle to inject the sample into the titrant/solvent solution in the titrator vessel. Then, liquid was drawn up into the syringe and reinjected into the titrator several times to wash any remaining sample into the titrator. This technique allowed single or two-phase samples to be analyzed for water without adding a third component to keep the water in solution. The titrant was calibrated by injecting weighed aliquots

Table 2. Gas Chromatographic Methods

item	details
	Ethylene Glycol Ethers
gas chromatograph	Hewlett-Packard 5890A with flame ionization detector
column	30 m × 0.32 mm i.d. DB-1 capillary column, 3-μm film thickness
oven program	oven temperature: varied with system, no ramping injector temperature: 250 °C detector temperature: 250 °C
gas flows	carrier: helium at 10 psig split ratio: adjusted with system to give desired separation
injection size	1.0 μL
	Propylene Glycol Ethers
gas chromatograph	Hewlett-Packard 6890 with thermal conductivity detector
column	30 m × 0.25 mm i.d. Zebron ZB-1 capillary column, 0.25-μm film thickness
oven program	initial temperature: 50 °C rate: 10 °C/min final temperature: 250 °C for 10 min injector temperature: 250 °C detector temperature: 250 °C
gas flows	carrier: helium at 10 psig split ratio: 200/1
injection size	1.0 μL

of pure water in triplicate. The composition of water in the standards and in the samples was repeatable to better than 1% of the measured value. The composition of the glycol ether from the GC and the composition of water from the Karl Fisher titrator were then added together and normalized to obtain the composition of the phase. The unnormalized sums of the two compositions found by the independent methods typically added up to (99 to 101) mass %.

For mixtures where the minor component was quite insoluble in water, large samples, (10 to 20) g, of the aqueous phase were taken into weighed glass vials. A known mass of a mixture of toluene and ethylbenzene was added to each vial, and the minor component was extracted into the toluene-rich phase by vigorously shaking the vial. Ethylbenzene served as an internal standard. An aliquot of the toluene-rich phase was then analyzed by gas chromatography. Because water typically was 99 mass % or more of the original sample, its concentration was found by difference.

The hydrocarbon-rich samples were analyzed for water by Karl Fisher titration using the technique outlined above. If the composition of water in the organic phase was less than approximately 30 mass %, the composition of the glycol ether was found by difference. Otherwise, samples were taken and analyzed by gas chromatography. The two compositions were then added together and normalized to obtain the composition of the phase. The unnormalized sums of the two compositions found by the independent methods typically added up to (99 to 101) mass %.

Water + Propylene Glycol Ether Systems. Test samples were prepared by mixing 10 g glycol ether with 10 g water (with weights recorded to four decimal places) in 50 mL graduated centrifuge tubes with conical bottoms. The tubes were sealed with polyethylene-lined caps, shaken vigorously by hand for about 1 min, and then placed in a specially designed rack inside a thermostatically controlled, recirculating water-propylene glycol bath at the desired test temperature (within an uncertainty of ±0.1 °C) with the tops of the tubes extending out of the bath liquid. All experiments with water + propylene glycol ether systems were conducted at atmospheric pressure. After 15 min, each tube was removed from the bath, shaken vigorously for about 1 min, and then placed again in the bath. This procedure was repeated again 45 min later. The tubes were then left in the bath overnight or for a maximum of 24 h.

After the test time had elapsed, the tubes were shaken one more time and then left in the bath for an additional 15 min. Each vial was then visually examined to determine if the test mixture had formed a single-phase system, a two-phase system, or had frozen during the test. Freezing was observed in some mixtures of water + propylene glycol *n*-butyl ether and water + tripropylene glycol *n*-butyl ether at −10 °C. In cases where two phases were present, the tubes were briefly held out of the bath and the volume of each layer determined from the graduations in the tube. The vials were then sampled while in the bath at the test temperature. A disposable pipet was inserted very slightly and carefully into the top layer to withdraw about a pipet full or roughly (2 to 3) g from the top layer without disturbing the bottom layer. The sample withdrawn was placed into a tared 10-mL vial with a polyethylene-lined cap. The sample mass was recorded to four decimal places and the vial sealed and labeled appropriately. Another pipet was then introduced into the conical bottom of the tube to sample the bottom layer. Air was constantly squeezed out of the pipet while passing the pipet through the residual top layer. The pipet bulb was also squeezed slightly while withdrawing the pipet from the tube to push some of the bottom layer out while going through the top layer. This procedure prevented serious contamination of the bottom layer sample with the top layer. Once withdrawn, the sample was delivered into another tared vial without touching the vial with the pipet and processed similarly to the top layer sample.

To achieve homogeneity, because most of the samples collected separated into two layers upon standing at room temperature, the samples were diluted with tetrahydrofuran (THF) in a 5:1 mass ratio (THF to sample). The required amount of THF was weighed directly into the tared vial containing the original sample in order not to change the original sample composition. The THF mass was also recorded to four decimal places. The diluted samples were then transferred to gas chromatograph vials and analyzed by the thermal conductivity detector of a Hewlett-Packard 6890 Series gas chromatograph. The column used was a 30 m × 0.25 mm i.d. Zebron ZB-1 capillary column from Phenomenex with a 0.25 μm film thickness. Details of the gas chromatographic method are given in Table 2.

THF was used as diluent, internal standard, and reference solvent. Standards were prepared containing (5, 50, and 95) % by mass of each glycol ether in water. THF was added to these standards in the same 5:1 mass ratio used in the sample collection step. All masses were recorded to four decimal places. The calibration was mostly linear within the range of standards used. The 95% or the 5% standards were used to set up the initial calibration runs preceding the analysis of the actual samples. Recalibrations were conducted as needed to achieve a ±5% analytical precision. All samples were run in triplicate and the results averaged.

Results and Discussion

The overall uncertainty in the measured compositions, based on the repeatability of the gas chromatographic methods, error in the sampling technique, and the uncertainty in temperature, is estimated to be less than ±5% of

Table 3. Measured Equilibrium Temperatures and Mutual Solubility for Water + Ethylene Glycol *n*-Butyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
50.0	18.8	41.6
55.0	13.6	50.0
60.0	11.8	54.1
70.0	10.2	58.3
80.0	9.60	60.0
90.0	9.88	60.3
100.0	10.4	59.6
110.0	12.0	57.3
120.0	14.6	54.0
128.0	21.3	44.6

Table 4. Measured Equilibrium Temperatures and Mutual Solubility for Water + Ethylene Glycol *n*-Pentyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
20.0	3.64	71.1
40.0	2.62	77.1
60.0	2.29	79.6
80.0	2.17	80.3

Table 5. Measured Equilibrium Temperatures and Mutual Solubility for Water + Diethylene Glycol *n*-Pentyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
40.4	phase boundary	31.2
45.0	5.38	46.7
50.0	4.18	55.9
60.0	3.42	63.8
80.0	2.96	71.0
100.0	3.00	73.4

Table 6. Measured Equilibrium Temperatures and Mutual Solubility for Water + Ethylene Glycol 2-Methyl-1-Butyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
20.0	3.65	81.4
40.0	2.70	83.6
60.0	2.39	84.3
80.0	2.31	84.2

Table 7. Measured Equilibrium Temperatures and Mutual Solubility for Water + Diethylene Glycol 2-Methyl-1-Butyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
30.2	phase boundary	20.8
30.4	phase boundary	29.2
32.0	8.57	41.1
40.0	4.71	58.5
60.0	3.51	71.8
80.0	2.98	76.0

the reported value. Available comparisons with published data are generally within 2 to 5%.

Table 8. Measured Equilibrium Temperatures and Mutual Solubility for Water + Ethylene Glycol *n*-Hexyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
20.0	0.946	82.3
40.0	0.743	84.4
60.0	0.683	86.0
80.0	0.693	86.3

Table 9. Measured Equilibrium Temperatures and Mutual Solubility for Water + Diethylene Glycol *n*-Hexyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
20.0	1.99	46.6
40.0	1.30	70.1
60.0	0.996	76.2
80.0	0.949	79.8

Table 10. Measured Equilibrium Temperatures and Mutual Solubility for Water + Triethylene Glycol *n*-Hexyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
50.0	2.31	40.0
60.0	1.43	56.9
70.0	1.29	65.5
80.0	1.21	70.7
90.0	1.21	73.8
100.0	1.25	75.9
110.0	1.29	76.9
120.0	1.36	77.3
130.0	1.50	77.5

Table 11. Measured Equilibrium Temperatures and Mutual Solubility for Water + Ethylene Glycol *n*-Heptyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
30.0	0.247	86.5
40.0	0.214	87.5
60.0	0.207	88.8
80.0	0.227	89.2
100.0	0.268	89.2

Table 12. Measured Equilibrium Temperatures and Mutual Solubility for Water + Diethylene Glycol *n*-Heptyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
20.0	0.517	58.4
30.0	0.420	65.6
40.0	0.355	72.6
60.0	0.313	80.4
80.0	0.308	83.6
100.0	0.359	84.9

Tables 3−13 give the measured equilibrium compositions for the 11 water + ethylene glycol ether systems; these data are plotted in Figures 1−11. Several investigators have reported measurements of phase compositions for the water + ethylene glycol *n*-butyl ether system for at least a portion of the closed-loop liquid−liquid equilibrium phase diagram.[11−15] The mutual miscibility curves and the LCST and UCST are well established, with generally good agreement among researchers. Figure 1 shows a comparison of the data of the present study with the data of Ellis,[16] which are representative of the literature; excellent agreement is observed between the two data sets.

For the water + ethylene glycol *n*-hexyl ether system, a single set of data is available for comparison. Figure 6 is a plot of the data from this study along with the data of Stephenson;[14] good agreement is obtained.

Published data for the mutual solubility of the water + diethylene glycol *n*-hexyl ether system do not all agree. The data of Lee and Lee[12] and Chakhovsky[17] extend to a lower critical solution temperature at least 10° below the LCST

Table 13. Measured Equilibrium Temperatures and Mutual Solubility for Water + Triethylene Glycol *n*-Heptyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
29.1	phase boundary	19.0
30.0	1.33	22.9
40.0	0.535	46.6
50.0	0.438	56.8
60.0	0.417	65.5
80.0	0.396	76.4
100.0	0.411	80.0

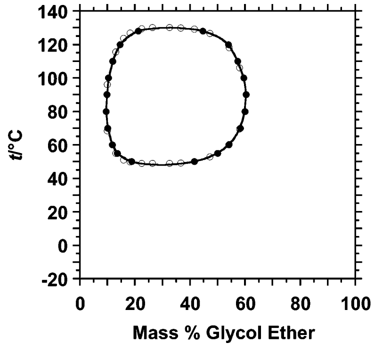

Figure 1. Mutual Solubility for Water + Ethylene Glycol *n*-Butyl Ether: ● This work; ○ Ellis (1967).

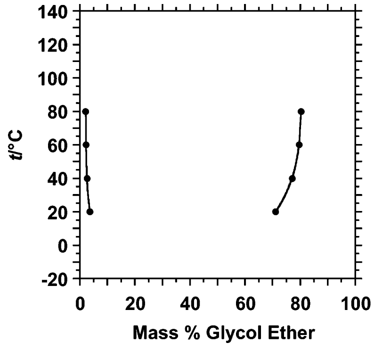

Figure 2. Mutual Solubility for Water + Ethylene Glycol *n*-Pentyl Ether.

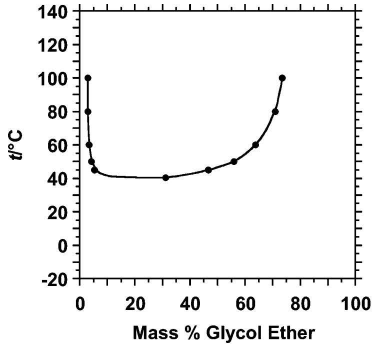

Figure 3. Mutual Solubility for Water + Diethylene Glycol *n*-Pentyl Ether.

reported by Lai and Chen,[18] Stephenson,[14] and Lim et al.[19] In Figure 7, the data from this study are shown to agree well with the data of Lai and Chen,[18] which are also in good agreement with the mutual solubility data of Stephenson[14] and Lim et al.[19]

Data in the literature for the water + triethylene glycol *n*-hexyl ether system consist of two plots of the two-phase boundary with reported LCST's of 46.0 °C[20] and 44.66 °C,[21] and mutual solubility data with a reported LCST of 44.09 °C.[18] Good agreement is shown in Figure 8 between the mutual solubility data of this study and that of Lai and Chen.[18]

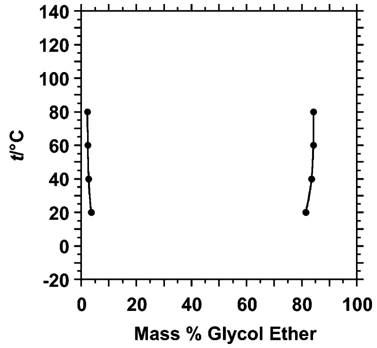

Figure 4. Mutual Solubility for Water + Ethylene Glycol 2-Methyl-1-Butyl Ether.

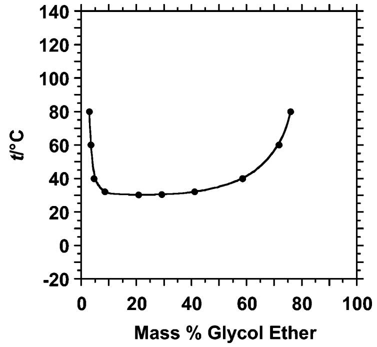

Figure 5. Mutual Solubility for Water + Diethylene Glycol 2-Methyl-1-Butyl Ether.

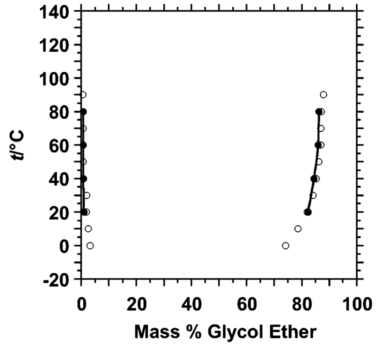

Figure 6. Mutual Solubility for Water + Ethylene Glycol *n*-Hexyl Ether: ● This work; ○ Stephenson (1993).

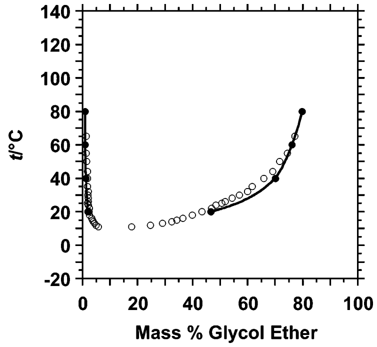

Figure 7. Mutual Solubility for Water + Diethylene Glycol *n*-Hexyl Ether: ● This work; ○ Lai and Chen (1999).

A single set of data[18] is available for comparison with the data of this study for the water + triethylene glycol *n*-heptyl ether system; these are plotted together in Figure

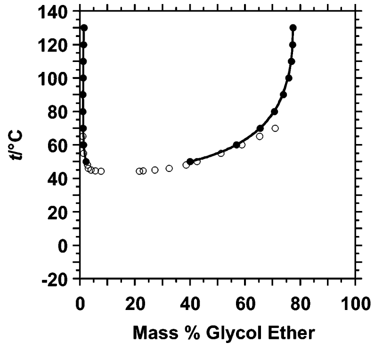

Figure 8. Mutual Solubility for Water + Triethylene Glycol *n*-Hexyl Ether: ● This work; ○ Lai and Chen (1999).

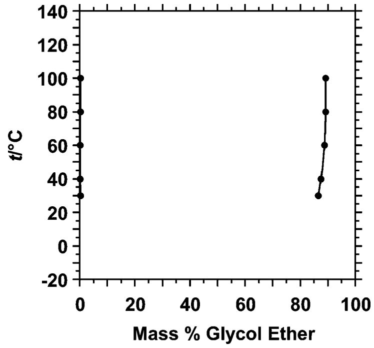

Figure 9. Mutual Solubility for Water + Ethylene Glycol *n*-Heptyl Ether.

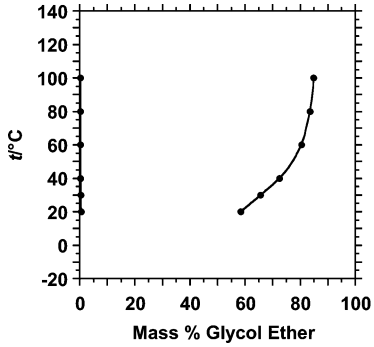

Figure 10. Mutual Solubility for Water + Diethylene Glycol *n*-Heptyl Ether.

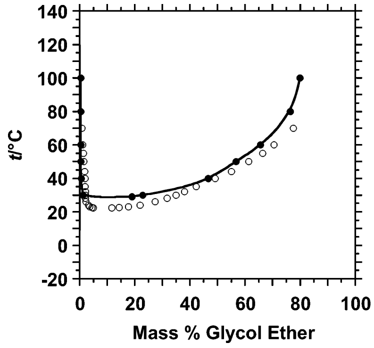

Figure 11. Mutual Solubility for Water + Triethylene Glycol *n*-Heptyl Ether: ● This work; ○ Lai and Chen (1999).

11. The data of Lai and Chen[18] dip lower in temperature than those of this study and give a LCST (22.24 °C) almost 7 °C lower than that estimated by the mutual solubility data of this study. This size of discrepancy in the LCST could be significant in an application using the inverse solubility behavior of this system at ambient temperature.

Table 14. Measured Equilibrium Temperatures and Mutual Solubility for Water + Propylene Glycol *n*-Propyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
32.0	one phase	53.7
33.0	36.4	57.4
36.0	28.0	62.9
37.0	25.7	64.0
42.0	24.0	68.6
60.0	18.5	73.8
65.0	16.9	74.5

Table 15. Measured Equilibrium Temperatures and Mutual Solubility for Water + Dipropylene Glycol *n*-Propyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
10.0	one phase	48.0
15.0	29.1	69.7
20.0	20.2	74.2
30.0	13.0	80.0
40.0	9.32	87.3
60.0	5.44	92.9

Table 16. Measured Equilibrium Temperatures and Mutual Solubility for Water + Tripropylene Glycol *n*-Propyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
0.0	one phase	51.5
10.0	25.7	75.4
20.0	16.5	93.5
30.0	11.3	96.2
40.0	6.84	98.7
60.0	3.36	96.4

Table 17. Measured Equilibrium Temperatures and Mutual Solubility for Water + Propylene Glycol *n*-Butyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
−5.0	11.5	73.5
0.0	9.35	76.6
12.0	7.60	81.2
22.0	6.91	83.6
25.0	5.50	84.1
32.0	5.00	84.7
40.0	3.27	84.2
48.0	3.30	85.7
60.0	3.19	88.8

The source of the discrepancy is unknown, although in this case the results may be particularly sensitive to the presence of impurities. The triethylene glycol *n*-heptyl ether sample used in the present study was 99% pure, and the sample used in the Lai and Chen study was reported to have a nominal purity of 98%.

Tables 14−19 give the measured equilibrium compositions for the six water + propylene glycol ether systems; these data are plotted in Figures 12−17. For these systems, a single source of published mutual solubility data exists for each of the following glycol ethers: propylene glycol *n*-propyl ether,[22] dipropylene glycol *n*-propyl ether,[22] tripropylene glycol *n*-propyl ether,[22] and propylene glycol *n*-butyl ether.[14] The literature data are plotted with the results of this study in Figures 12−15. Good agreement is obtained except for two data points from Davison et al.[22] in the water + propylene glycol *n*-propyl ether system and the data from Davison et al.[22] for the water + tripropylene glycol *n*-propyl

Table 18. Measured Equilibrium Temperatures and Mutual Solubility for Water + Dipropylene Glycol *n*-Butyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
−10.0	one phase	50.0
0.0	19.1	79.9
4.0	14.4	80.0
25.0	4.00	88.9
40.0	2.60	90.8
60.0	1.50	92.7
80.0	1.30	92.3

Table 19. Measured Equilibrium Temperatures and Mutual Solubility for Water + Tripropylene Glycol *n*-Butyl Ether

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
0.0	11.1	87.2
10.0	8.03	92.2
20.0	4.59	93.0
40.0	1.70	95.0
60.0	0.84	93.7

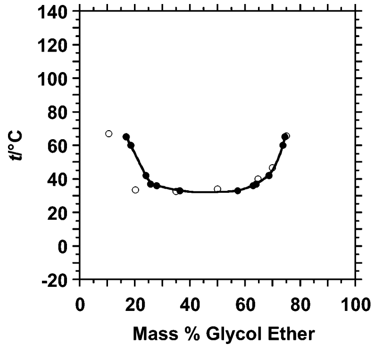

Figure 12. Mutual Solubility for Water + Propylene Glycol *n*-Propyl Ether: ● This work; ○ Davison et al. (1966).

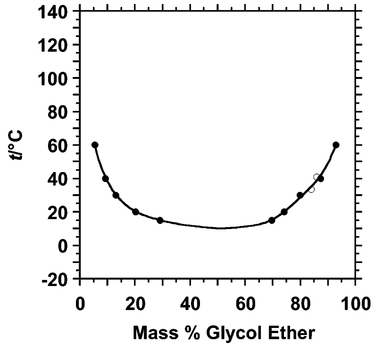

Figure 13. Mutual Solubility for Water + Dipropylene Glycol *n*-Propyl Ether: ● This work; ○ Davison et al. (1966).

ether system (two points). One reason for the discrepancy between the data of Davison et al. and the data of the present study could be a difference in purity of glycol ether used, particularly in the water + tripropylene glycol *n*-propyl ether system. The tripropylene glycol *n*-propyl ether used in this study was among the least pure (95.0%) of the glycol ethers used. The glycol ethers used by Davison et al. were fractionally distilled from the reaction products of propylene oxide and *n*-propanol; while boiling point ranges of the resulting fractions are given, purity is not specified.[23]

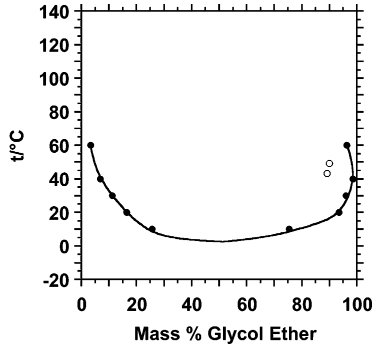

Figure 14. Mutual Solubility for Water + Tripropylene Glycol *n*-Propyl Ether: ● This work; ○ Davison et al. (1966).

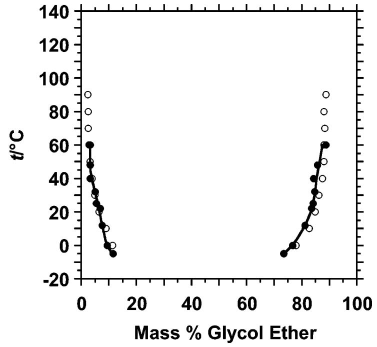

Figure 15. Mutual Solubility for Water + Propylene Glycol *n*-Butyl Ether: ● This work; ○ Stephenson (1993).

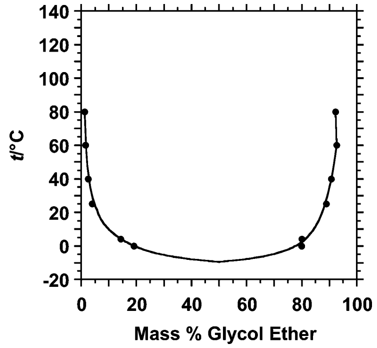

Figure 16. Mutual Solubility for Water + Dipropylene Glycol *n*-Butyl Ether.

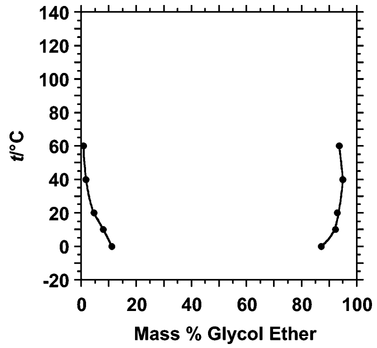

Figure 17. Mutual Solubility for Water + Tripropylene Glycol *n*-Butyl Ether.

A literature search disclosed no previous mutual solubility data for the water + glycol ether systems containing the following glycol ethers: ethylene glycol *n*-pentyl ether, diethylene glycol *n*-pentyl ether, ethylene glycol 2-methyl-1-butyl ether, diethylene glycol 2-methyl-1-butyl ether, ethylene glycol *n*-heptyl ether, diethylene glycol *n*-heptyl ether, dipropylene glycol *n*-butyl ether, and tripropylene glycol *n*-butyl ether.

For several systems, the mutual solubility data are extensive enough to allow a smooth curve to be fitted

Table 20. Lower Critical Solution Temperature (LCST) Estimated from Mutual Solubility Data for Water + Glycol Ether Systems

system	LCST/°C
water + ethylene glycol *n*-butyl ether	48
water + diethylene glycol *n*-pentyl ether	40
water + diethylene glycol 2-methyl-1-butyl ether	30
water + triethylene glycol *n*-heptyl ether	29
water + propylene glycol *n*-propyl ether	32
water + dipropylene glycol *n*-propyl ether	10
water + tripropylene glycol *n*-propyl ether	2
water + dipropylene glycol *n*-butyl ether	−10

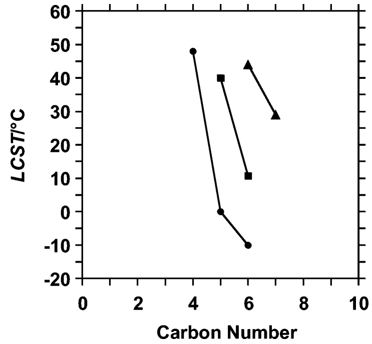

Figure 18. LCST Versus Carbon Number for *n*-Alkyl Ethylene Glycol Ethers: ● Mono-; ■ Di-; ▲ Triethylene glycol ethers.

through the data giving the entire lower consolute curve and an estimate of the LCST. Table 20 gives the water + glycol ether systems for which an LCST has been estimated (to the nearest 1 °C) from the mutual solubility data of this study. For the water + ethylene glycol *n*-butyl ether system, an upper critical solution temperature (UCST) was similarly estimated; its value is 130 °C.

The measurements of this study show that addition of oxyethylene groups increases the hydrophilicity of the glycol ether molecule. This effect can perhaps best be seen in the plots of the data for the ethylene glycol *n*-hexyl ether series, Figures 6−8. As oxyethylene groups are added to ethylene glycol *n*-hexyl ether, the two-phase immiscibility shrinks in size at a given temperature and the LCST increases in temperature. This trend is also shown in Figure 18, which plots the LCST for selected mono-, di-, and triethylene glycol ethers as a function of carbon number in the *n*-alkyl end group. The LCST data reported by Lai and Chen for the water + diethylene glycol *n*-hexyl ether (10.79 °C) and water + triethylene glycol *n*-hexyl ether (44.09 °C) systems[18] were used in Figure 18 along with estimations of the LCST for the water + ethylene glycol *n*-pentyl ether system (0 °C) and the water + ethylene glycol *n*-hexyl ether system (−10 °C).

In contrast to the ethylene glycol ethers, adding an oxyalkylene group to the propylene glycol ethers increases the hydrophobicity of the molecule. The increase in oxypropylene groups from one to three in the propylene glycol *n*-propyl ether series results in an increasingly wider immiscibility gap at a given temperature and an increasingly lower temperature for the observed LCST (see Figures 12−14). A corresponding increase in the composition range of immiscibility is observed as oxypropylene groups are added in the propylene glycol *n*-butyl ether series in Figures 15−17. The expected decrease in LCST with added PO groups cannot be definitively seen from the Figures, however, because of the LCST extending to temperatures below the measurement range of this study. Figure 19 is a plot of LCST for selected mono-, di-, and tripropylene glycol ethers as a function of carbon number in the *n*-alkyl end group, which shows the general trend of a decreasing LCST with increasing oxypropylene groups. In Figure 19, an estimated LCST (−10 °C for both) for the water + propylene glycol *n*-butyl ether system and the water + tripropylene glycol *n*-butyl ether system was used.

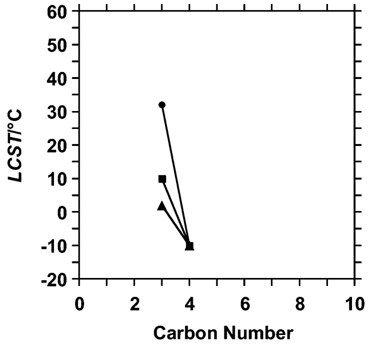

Figure 19. LCST Versus Carbon Number for *n*-Alkyl Propylene Glycol Ethers: ● Mono-; ■ Di-; ▲ Tripropylene glycol ethers.

It is interesting that poly(ethylene glycol)s (PEGs) do not exhibit the same trend as ethylene glycol ethers with regard to change in LCST with the addition of oxyethylene groups. As the number of oxyethylene groups in the PEG polymer chain increases (and thus molecular weight increases), the LCST decreases.[24,25] This comparison shows that glycol ethers are not simply low molecular weight analogues of polyglycols, as they do not exhibit all of the same trends in physical properties.

For water + glycol ether liquid mixtures, whether hydrophobic or hydrophilic interactions dominate depends strongly upon temperature and structure. The LCST is the temperature at which the hydrophobic and hydrophilic interactions are balanced for the particular water + glycol ether system. For glycol ethers containing an *n*-alkyl group, the mutual solubility data show that the LCST increases with a decrease in the carbon number of the end group because of decreasing hydrophobic character (see Figures 18 and 19). The data also show that branched alkyl end groups are more hydrophobic (exhibiting lower LCST values) than linear alkyl end groups (compare the mutual solubility of the water + diethylene glycol 2-methyl-1-butyl ether system, Figure 5, with that for the water + diethylene glycol *n*-pentyl ether system, Figure 3). Also, the LCST for a given ethylene glycol ether is higher than that for the corresponding propylene glycol ether analogue because of the difference in hydrophobic character of R = H versus R = CH_3 attached to the backbone of the molecule.

Certain combinations of hydrophobic and hydrophilic end groups can produce glycol ethers for which the LCST of the water + glycol ether system is near room temperature. The systems water + diethylene glycol 2-methyl-1-butyl ether, water + triethylene glycol *n*-heptyl ether, and water + propylene glycol *n*-propyl ether all have an LCST within 10 °C of 25 °C; these systems may be particularly useful in applications designed for implementation at typical indoor ambient temperature.

The LCST of water + glycol ether systems can also be manipulated by mixing glycol ethers. Table 21 lists mutual solubility measurements for a water + glycol ether system in which the glycol ether is an equimolar mixture of propylene glycol *n*-propyl ether and dipropylene glycol *n*-propyl ether. The results are compared to those for the pure component glycol ether systems in Figure 20. As seen in Figure 20, the mutual solubility curve of the mixture falls between those of the pure components. The LCST for the equimolar mixture (40.1 mass % propylene glycol

Table 21. Measured Equilibrium Temperatures and Mutual Solubility for Water + an Equimolar Mixture of [Propylene Glycol *n*-Propyl Ether + Dipropylene Glycol *n*-Propyl Ether]

	mass % glycol ether	
t/°C	lower liquid phase	upper liquid phase
17.8	phase boundary	39.2
20.0	27.5	65.2
30.0	17.2	76.0
40.0	12.9	79.9
50.0	10.1	81.9
60.0	8.53	83.0
80.0	6.52	84.0
100.0	5.92	84.0

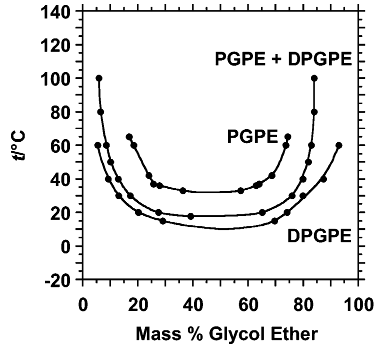

Figure 20. Mutual Solubility for Water + [Equimolar Mixture of Propylene Glycol *n*-Propyl Ether + Dipropylene Glycol *n*-Propyl Ether] Compared with Mutual Solubility Curves for Water + Propylene Glycol *n*-Propyl Ether (PGPE) and Water + Dipropylene Glycol *n*-Propyl Ether (DPGPE).

n-propyl ether, 59.9 mass % dipropylene glycol *n*-propyl ether), 18 °C, is close to the weighted average for the pure component systems, 19 °C.

Acknowledgment

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