Mutual Solubility of Water and Glycerol and Glycol Ethers

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Mutual solubility data are presented for water and a variety of glycol and glycerol ethers. The solubility of the glycerol ethers with water varies with molecular structure in a manner similar to amines and water, but the effect is less pronounced in the ethers than in the amines.

THE solubility characteristics of a number of glycol and glycerol ethers were investigated in a search for suitable desalination solvents. The solubility of water in the solvent should range from about 30% to less than 10% over a narrow temperature span. This property is found principally in solvent-water systems having lower consolute temperatures, which in general result from the interaction of large negative enthalpies and entropies of solution. These properties in turn result from specific interactions such as hydrogen bonding, which are sensitive to relatively slight changes in molecular structure.

EXPERIMENTAL

All of the compounds investigated were synthesized for this work. The methods of syntheses and the product purity have been reported (*3*). The solubilities were measured by cloud points in sealed tubes, method 1; cloud points by titration, method 2; or Karl Fischer analysis.

In method 1, solutions were made up for a variety of con-concentrations by weight and sealed in glass tubes. These were totally immersed in a water bath and cloud points observed as the bath temperature was raised. In method 2 a known weight of one component was placed in a test tube in the bath and the other component was titrated into the

Table I. Solubility of Glycerol Ethers

($ROCH_2CHOHCH_2OR'$)

Method	H_2O, %	Temp., ° C.
Ethyl *n*-Propyl Glycerol Ether		
1	15.8	56.3
	16.6	49.3
	16.8	47.4
	19.5	35.9
	24.3	20.4
	29.2	13.9
	75.6	Immisc. to 0° C.
	85.3	21.4
	89.3	23.9
Ethyl Isopropyl Glycerol Ether		
1	19.3	70.6
	20.8	56.8
	23.7	50.4
	29.7	40.4
	39.9	36.1
	50.1	34.8
	59.8	34.1
	70.3	35.7
	80.1	48.8
	85.0	56.5
	89.7	78.4
Methyl *n*-Butyl Glycerol Ether		
1	20.3	87
	25.1	60
	29.9	50.5
	35.0	45
	41.2	41.5
	45.4	39.5
	88.9	37
	92	53
	93.5	58
	96	80
Ethyl *n*-Butyl Glycerol Ether		
2	10.5	78
	10.9	44.9
	11.6	33.4
	12.5	27.3
	94.6	28.4
	96.6	45.4
	97.7	72.6
Methyl *tert*-Butyl Glycerol Ether		
1	19.2	Misc. to 130° C.
	25.4	75.3
	29.9	66.3
	40.3	56.5
	50.4	53.8
	60.5	48.7
	65.0	43.3
	69.8	19.3
	75.0	21.4
	80.6	22.4
	85.0	24.3
	89.7	27.9
	95.7	47.8
Diisopropyl Glycerol Ether		
1	10	65
	13.3	31
	15.1	22
	16.7	14.5
	89.2	21
	93.1	30
	94.9	47
	96.1	59
Methyl *n*-Amyl Glycerol Ether		
1	12.2	Misc. to 130° C.
	14.4	56.7
	15.0	52.9
	16.6	44.4
	19.9	34.5
	24.6	26.7
	30.5	21.6
2	95.9	18.1
	96.6	27.4
	97.3	43.1
	97.7	56.4
	98.0	73.4
Methyl Isoamyl Glycerol Ether		
1	15.4	53.0
	21.0	30.0
	25.6	23.3
	30.7	18.3
	39.8	13.4
Methyl 2-Amyl Glycerol Ether		
1	10.9	Misc. to 130° C.
	14.2	37.6
	15.1	35.6
	19.8	25.9
2	94.5	28.6
	95.2	34.4
	96.4	48.8
	96.8	56.1
1,3-Dimethylbutoxypropanediol		
1	41.6	Misc. to 100° C.
	44.6	62.1
	47.9	47.7
	52.7	35.4
	57.8	27.8
	62.1	17.8
2	96.8	36.1
Ethyl *n*-Hexyl Oxyethyl Glycerol Ether		
2	9.8	80
	10.6	70
	11.4	60
	12.1	50
	12.9	40
	13.6	30
	14.1	20
	98.8	20
	99.1	30
	99.2	80

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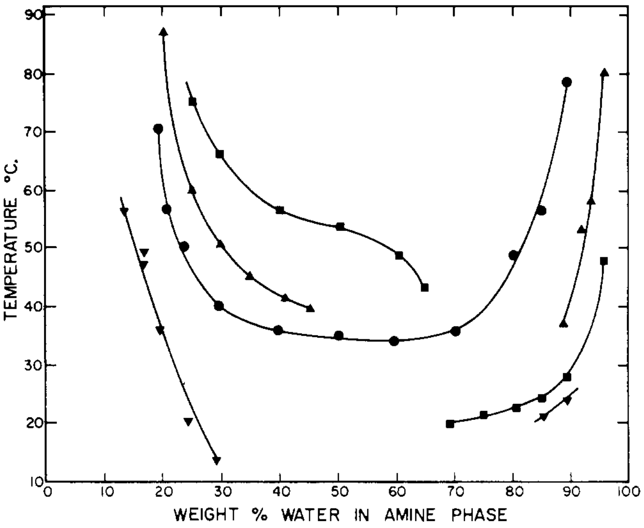

Figure 1. Solubility of eight-carbon-atom glycerol ethers

$ROCH_2CHOHCH_2OR'$

	R	R′
▼	ET	Pr
●	ET	1-Pr
▲	ME	BU
■	ME	*tert*-BU

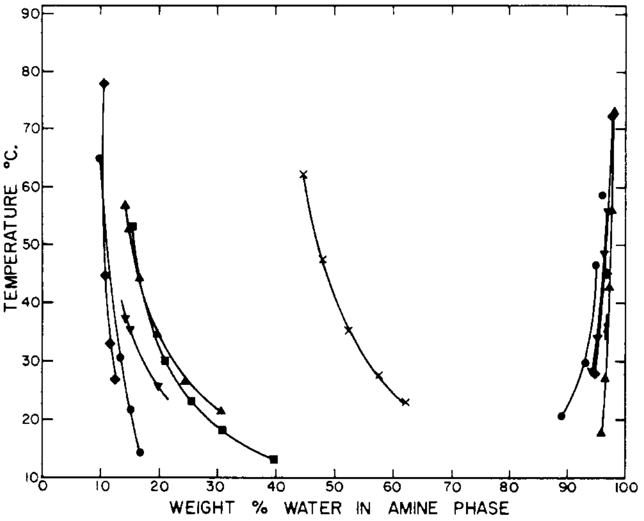

Figure 2. Solubility of nine-carbon-atom glycerol ethers

$ROCH_2CHOHCH_2OR'$

	R	R′
◆	ET	BU
●	i-Pr	i-Pr
▲	ME	AM
■	ME	i-AM
▼	M	2AM
X	H	1,2DiMEBU

tube slowly with mixing until a slight cloud prevailed. The procedure was continued as the bath temperature was lowered. The sealed tube cloud points are probably of higher accuracy, in that the concentrations were made up on an analytical balance. The approximate accuracy of the temperature measurements is indicated by the significant figures in Tables I and II. The lower accuracy is reported for compounds whose solubilities are lower and insensitive to temperature, making exact determination of the cloud point more difficult.

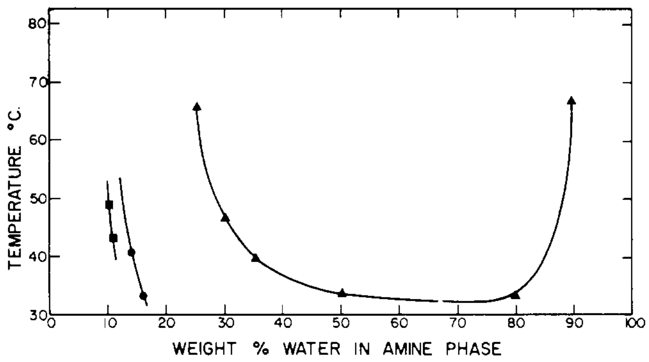

Figure 3. Solubility of propylene glycol *n*-propyl ethers

- ▲ Propylene glycol *n*-propyl ether
- ● Dipropylene glycol *n*-propyl ether
- ■ Tripropylene glycol *n*-propyl ether

Table II. Solubility of Glycol Ethers

(Mixed isomers)

Method	H_2O, %	Temp., °C.
Propylene Glycol *n*-Propyl Ether		
1	22.4	Misc. to 120° C.
	25.0	65.6
	30.1	46.7
	35.3	39.9
	50.0	33.9
	65.0	32.6
	79.8	33.5
	89.5	66.9
Dipropylene Glycol *n*-Propyl Ether		
1	11.2	Misc. to 120° C.
	14.0	40.9
	16.0	33.4
Tripropylene Glycol *n*-Propyl Ether		
1	8.9	Misc. to 120° C.
1	10.0	49.1
	10.8	43.1

DISCUSSION

Several structural patterns may be noted with the glycerol ethers in Figures 1 to 3. The principal effect is an increasing asymmetry in the solubility curve with increasing molecular asymmetry. The solubility of the solvent in water decreases as one alkyl group becomes large and thereby hydrophobic. On the other hand, the solubility of water in the solvent increases sharply in the series ($R = C_2$, $R' = C_4$), ($R = C_1$, $R' = C_5$), ($R = H$, $R' = C_6$). For R greater than ethyl the effect may diminish, as indicated by comparing ethyl butyl glycerol with diisopropyl glycerol. Actually two forces are operative in this example, as may be seen by comparing ethyl *n*-propyl glycerol with ethyl isopropyl glycerol. Branching in the α position of R or R′ probably increases solubility, but in comparing ethyl *n*-butyl glycerol to diisopropyl glycerol, branching and symmetry effects cancel. Branching and symmetry effects cooperating is seen with methyl *tert*-butyl glycerol. The peculiar shape of the solubility curve obtained for this compound is unexplained.

The effect of substituents on an amino nitrogen can be correlated in terms of steric and inductive effects (*1*, *2*). Branching in the α position increases the negativity of the active atom, N or O, and thus strengthens hydrogen bond formation. The effect is less pronounced in the glycerol ethers than in amines. Inductive forces are local, extending only about two or three atoms in an alkyl chain, and the active centers in the glycerol ethers consist of three separated oxygen atoms instead of a single nitrogen.

A final comparison may be made between ethyl butyl glycerol and ethyl *n*-hexyl oxyethyl glycerol. The water solubility in each solvent is nearly the same and so is the carbon-oxygen ratio in $-OC_4$ and $-OC_2OC_6$. Solvent solubility in water is much less for the compound having the larger alkyl group.

The solubility of a series of propylene glycol ethers is shown in Figure 3. In the series $R(C_3H_6O)_nOH$, the solubility decreases with increasing *n*, while with ethylene glycol ethers the opposite occurs.

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Dipole Moment of Sulfamic Acid and Viscosities of Its Solutions in Selected Nonaqueous Media

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Values of the dipole moment of sulfamic acid have been calculated from dielectric constant, density, and refractive index data for solutions of sulfamic acid in polar solvents using the Onsager and Wyman equations. Variation in the magnitude of the dipole moment with the solvent medium provides evidence of significant solvent effects. The change in viscosity with concentration also has been determined for solutions of sulfamic acid in each of the five nonaqueous media. All experimental data as a function of concentration have been fitted to appropriate equations.

SULFAMIC acid ($H_3N^+\text{-}SO_3^-$) in the solid state, like glycine, exists in a dipolar ionic form (*8*). In water it ionizes upon dissolution to yield an acid with strength comparable to that of nitric or hydrochloric acid. With most organic solvents, it is essentially insoluble or reacts chemically. In *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), and *N*-methyl-2-pyrrolidone (NM2PY), however, sulfamic acid is soluble to the extent of about 2 moles per liter without chemical reaction and yields solutions which are practically nonconducting. The dielectric and nonconducting properties of solutions in these three solvents indicate that the dipolar ionic form of sulfamic acid is retained.

Dielectric constant, density, and refractive index data have been determined for solutions of sulfamic acid in DMSO, DMA, NM2PY, and two DMSO-DMA mixtures in order that the dipole moment of sulfamic acid in each of these nonaqueous media may be evaluated. In addition, viscosities of the sulfamic acid solutions have been investigated to ascertain if a relationship exists between viscosity behavior and electrostriction effects.

EXPERIMENTAL

DMSO was purified by subjecting it to successive fractional freezings until a product with a constant maximum freezing point of 18.50° C. was obtained. Commercially available DMA and NM2PY were rendered anhydrous by azeotropic distillation with toluene. This was followed by fractional distillation at a pressure of 1 cm. through a 100-cm. column packed with glass helices. In each case the middle 60% of the product was retained. Values for several physical properties of each solvent are included in Table I. Sulfamic acid (purity assay of 99.99% by the G. Frederick Smith Chemical Co.) was stored in a desiccator over Anhydrone before use. Solutions in glass-stoppered flasks were prepared on a weight basis. Precautions were taken to minimize atmospheric contamination of the solutions during preparation and transferring.

The impedance bridge assembly, capacitance cells, temperature control, and principal aspects of the procedures for calibrating the cells and calculating the dielectric constants have been described in detail (*1, 2, 9*). The standard media used in the determination of cell constants were air and water, which have dielectric constants of unity and 78.30 (*10*), respectively, at 25° C. All capacitance measurements were made at 10 megacycles, after it had been confirmed that capacitance changes were independent of frequency in the 1- to 10-megacycle range.

The procedures for determining viscosities, densities, and refractive indices have been discussed adequately (*13, 14*).