Densities and Refractive Indices of Diethylene Glycol Ether–Water Solutions

Diethylene Glycol Monomethyl, Monoethyl, and Monobutyl Ethers

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FOLLOWING the work of Chu and Thompson (2) on densities and refractive indices of ethylene glycol monomethyl, monoethyl, and monobutyl ether–water solutions, similar data obtained for diethylene glycol monomethyl, monoethyl, and monobutyl ether are presented here. Purification and analytical procedures were identical with those described (2).

Refractive index data were determined at 20° and 25° C. and density data at 25° C. Values of these properties for pure diethylene glycol ethers have been reported (4); however, the data for diethylene glycol monoethyl ether are somewhat in doubt. No data have been given for aqueous solutions.

PURIFICATION AND PREPARATION OF SOLUTIONS

The water content, by weight, of the three purified products, as determined by means of Karl Fischer reagent, was as follows: diethylene glycol monomethyl ether 0.023%, diethylene glycol monoethyl ether 0.016%, and diethylene glycol monobutyl ether 0.006%. Within the experimental limits, the values for density and refractive index reported for the purified material are the same as for 100% pure diethylene glycol ethers obtained by extrapolating to zero water content. The data obtained for these purified diethylene glycol ethers may be compared with those previously reported (Table I). Because of the purification procedure followed in this work, present values are to be preferred. The earlier data for the specific gravity of diethylene glycol monoethyl ether seem much too low in comparison with either the authors' data or the supplier's specification for the unpurified material.

Solutions, with approximately 10 weight % increments to cover the entire composition range, were prepared as indicated earlier (2). Compositions were known to at least 1 part in 33,000 or 0.003 weight %.

DENSITY MEASUREMENTS

Solution densities were determined in 10-ml. Weld-type capped specific gravity bottles (2). Temperature was maintained at 25.00° ± 0.01° C. in a Fisher Isotemp constant temperature bath. The experimental results for aqueous solutions of all three diethylene glycol ethers are listed in Table II.

Based on the calibration of the specific gravity bottles, densities are known to within ±0.0001 gram per ml. The density-composition curves for diethylene glycol monomethyl and monoethyl ethers (Figure 1), which show definite maxima, resemble those for aqueous solutions of ethylene glycol monomethyl ether (2), propylene glycol (6), and dipropylene glycol (1). Near the maximum points of course, the change in density with composition is slight and analysis by density is not satisfactory. Diethylene glycol monobutyl ether has a density curve similar in shape to those for ethylene glycol monobutyl ether (2) and hexylene glycol (1).

REFRACTIVE INDEX MEASUREMENTS

Values of the refractive index were determined to 0.0001 (Figure 2 and Table II) using an improved precision Valentine refractometer with temperature controlled (at 20° or 25° C.) to ±0.01° C., as described (2).

Refractive index measurement allows determination of

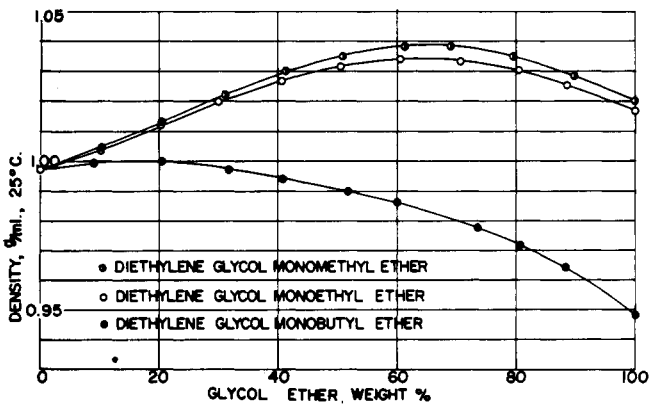

Figure 1. Densities of aqueous glycol ether solutions at 25° C.

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Table I. Properties of Pure Compounds

Compounds	Specific Gravity, 20°/20° C. Authors	Earlier data (4)	Earlier data (7)[a]	Density, 25° C., G./Ml. Authors	Refractive Index, n_D At 20° C. Authors	Earlier data (4)	At 25° C., Authors
Diethylene glycol monomethyl ether	1.02618	1.0211	1.0211	1.02004	1.4265	1.4263	1.4246
Diethylene glycol monoethyl ether	1.02337	0.9898	1.0273	1.01706	1.4295	1.4273	1.4275
Diethylene glycol monobutyl ether	0.95453	0.9536	0.9536	0.94844	1.4320	1.4316	1.4299

[a] Union Carbide data for materials as received.

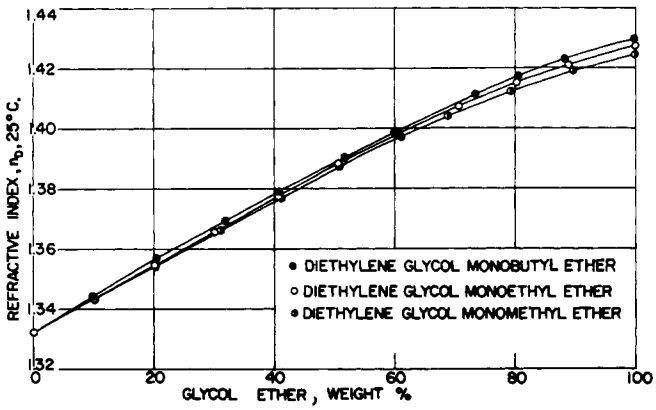

Figure 2. Refractive indices of aqueous glycol ether solutions at 25° C.

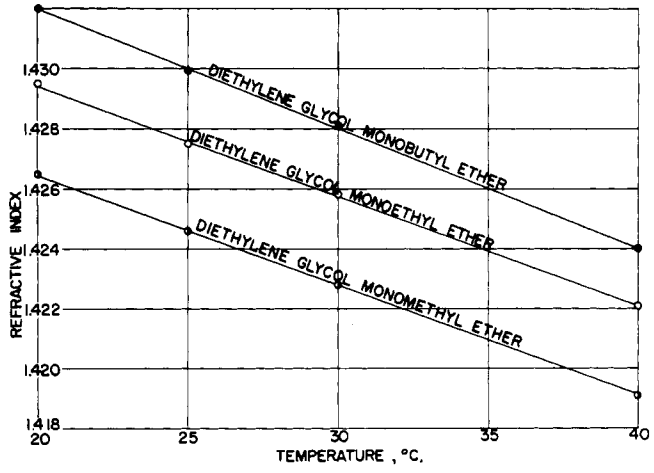

Figure 3. Effect of temperature on refractive index of pure glycol ethers

the glycol ether content to approximately ±0.14% or better for solutions of all three diethylene glycol ethers.

Variation in refractive index with temperature for the three purified glycol ethers is shown in Figure 3. Within the experimental limits of measurements, all three compounds indicate a linear change in refractive index with temperature over the range from 20° to 40° C.

Application of the Eykman equation, as recommended by Dreisbach (*3*), was tested for these compounds. The Eykman equation is given by:

$$\frac{n^2-1}{n+0.4} \times \frac{1}{d} = C_1$$

where n is the refractive index, d is the density, and C_1 is a constant. For all three glycol ethers at 20° and 25° C. the equation was found to give excellent checks as indicated by the values of C_1 given in Table III.

The simple equation suggested by Ward and Kurtz (*8*) $\Delta n = 0.6\ \Delta d$, for correcting the refractive index of hydrocarbons for small changes in temperature was not found to be satisfactory for the glycol ethers investigated.

Table II. Experimental Data

Solutions	Wt. %	Abs. Density, G./Ml. at 25° C.	Refractive Index, n_D At 20° C.	At. 25° C.
		Diethylene Glycol Monomethyl Ether		
Pure water	0	0.99707(*5*)	1.3330	1.3325
1	10.49	1.0049	1.3441	1.3434
2	20.44	1.0131	1.3550	1.3543
3	31.20	1.0220	1.3672	1.3662
4	41.14	1.0295	1.3783	1.3770
5	50.90	1.0349	1.3888	1.3874
6	61.14	1.0381	1.3988	1.3973
7	68.98	1.0381	1.4058	1.4042
8	79.44	1.0350	1.4141	1.4124
9	89.84	1.0286	1.4209	1.4191
Purified material (0.023% H_2O)		1.0200	1.4265	1.4246
		Diethylene Glycol Monoethyl Ether		
Pure water	0	0.99707(*5*)	1.3330	1.3325
1	10.15	1.0041	1.3441	1.3434
2	20.12	1.0120	1.3554	1.3545
3	30.06	1.0196	1.3669	1.3659
4	40.62	1.0268	1.3792	1.3776
5	50.53	1.0318	1.3897	1.3882
6	60.63	1.0339	1.3998	1.3982
7	70.76	1.0334	1.4091	1.4073
8	80.31	1.0304	1.4168	1.4151
9	88.86	1.0255	1.4228	1.4210
Purified material (0.016% H_2O)		1.0171	1.4295	1.4275
		Diethylene Glycol Monobutyl Ether		
Pure water	0	0.99707(*5*)	1.3330	1.3325
1	9.90	0.9991	1.3453	1.3445
2	20.43	0.9993	1.3580	1.3570
3	31.78	0.9969	1.3709	1.3695
4	40.76	0.9942	1.3805	1.3790
5	51.71	0.9900	1.3922	1.3906
6	60.06	0.9862	1.4007	1.3987
7	73.46	0.9778	1.4130	1.4112
8	80.67	0.9719	1.4193	1.4174
9	88.29	0.9642	1.4250	1.4230
Purified material (0.006% H_2O)		0.9484	1.4320	1.4299

Table III. Applicability of Eykman Equation

Compound	Value of C_1 At 20° C.	At 25° C.
Diethylene glycol monomethyl ether	0.5531	0.5532
Diethylene glycol monoethyl ether	0.5584	0.5584
Diethylene glycol monobutyl ether	0.6019	0.6019

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