Densities and Refractive Indices of Glycol Ether–Water Solutions

Ethylene Glycol Monomethyl, Monoethyl, and Monobutyl Ethers

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TO PROVIDE a simple but precise method for analyzing glycol ether-water mixtures, the densities and refractive indices of ethylene glycol monomethyl ether (2-methoxyethanol), $CH_3OCH_2CH_2OH$, ethylene glycol monoethyl ether (2-ethoxyethanol), $C_2H_5OCH_2CH_2OH$, and ethylene glycol monobutyl ether (2-butoxyethanol), $C_4H_9OCH_2CH_2OH$, were determined at 25° C. over the entire composition range and refractive index data at 20° C. were also obtained. Although values of these properties have been reported in the literature (*2, 3, 5, 9*) for the pure glycol ethers, no data have been given for aqueous solutions.

PURIFICATION OF MATERIALS

The three pure grade glycol ethers were fractionated using a reflux ratio of 25 to 1 in an adiabatically operated packed column (1 inch in diameter and packed to a depth of 36 inches with 3/16-inch glass helices). The distillations were carried out in an entirely closed system. Only the middle portion (20 to 90%) of the constant boiling distillate was collected for making up the solutions. Reproducibility of the products was adequate, as shown by the constancy of the physical properties. The purified glycol ethers contained small amounts of water as determined by means of Karl Fischer reagent. The water contents, by weight, of the three purified products were as follows: ethylene glycol monomethyl ether 0.05%, ethylene glycol monoethyl ether 0.06%, and ethylene glycol monobutyl ether 0.04%. The density and refractive index reported for 100% pure glycol ethers were obtained by extrapolating the data to zero water content. The data for these pure glycol ethers give excellent checks with those previously reported as shown in Table I.

PREPARATION OF SOLUTIONS

For each of the glycol ethers, the purified material and freshly boiled demineralized water (with a specific conductivity of approximately 10^{-6} ohm^{-1} cm.$^{-1}$) were used to prepare nine solutions of various glycol ether concentrations from 10 to 90 weight %.

These solutions of known composition were prepared by injecting approximate amounts of purified glycol ethers and water into dried, stoppered, tared, 60-ml. vaccine bottles from a buret, the top of which was equipped with a drying tube containing anhydrous activated alumina. The exact compositions were determined by weighing to 0.1 mg. The burets used to transfer the glycol ethers were dried at 110° C., promptly connected with a drying tube, and allowed to cool until used.

All solution compositions, based on amounts of material weighed and accuracy of the weighings, were known to 1 part in 46,000 or better than ±0.002 weight %.

DENSITY MEASUREMENTS

Density was measured in 10-ml. Weld-type capped, specific gravity bottles which had been calibrated using boiled demineralized water. The bottles were submerged to near the top of the stem in a Fisher Isotemp constant temperature bath maintained at 25.00° ± 0.01° C., as determined by a calibrated thermometer. Duplicate determinations were made on each solution. All weighings were reduced to values in vacuo, and the absolute densities at 25° C. were calculated as grams per milliliter. Expressed in these units, the density is numerically equal to the specific gravity at 25° C. compared to water at its maximum density (3.98° C.).

The experimental results for aqueous solutions of all three glycol ethers are listed in Table II. Smoothed values, at even composition increments, obtained from a large scale plot similar to Figure 1, are presented in Table III.

The maximum error resulting from uncertainties in the volume calibration of the specific gravity bottles was ±0.0001 gram per ml. Because of the shape of the density-composition curves, the usefulness of the density measurements for analytical purposes varies with the glycol ether concentration. The curves for both ethylene glycol monomethyl ether and ethylene glycol monoethyl ether, which show maxima are somewhat similar to that found for propylene glycol–water and dipropylene glycol–water solutions by MacBeth and Thompson (*8*) and Chiao and Thompson (*1*), respectively. In the vicinity of the maximum in each of

Table I. Properties of Pure Compounds

	Refractive Index, n_D					Specific Gravity			
	At 20° C.		At 25° C.			20° C./20° C.	25° C./25° C.		Density at 25° C., G./Ml.,
	Authors	Earlier data (*2, 5*)	Authors	Earlier Data (*9*)	Earlier Data (*3*)	Earlier data (*3, 5*)	Authors	Earlier data (*3*)	Authors
Ethylene glycol monomethyl ether	1.4021	1.4021	1.4002	...	1.400	0.9663	0.96306	0.963	0.96024
Ethylene glycol monoethyl ether	1.4077	1.4076	1.4057	1.4050	1.406	0.9311	0.92791	0.928	0.92520
Ethylene glycol monobutyl ether	1.4193	1.4193	1.4173	1.4169	1.417	0.9019	0.89927	0.899	0.89664

Table II. Experimental Data

	Wt. %	Abs. Density, G./Ml. at 25° C.	R. I., n_D At 20° C.	R. I., n_D At 25° C.
		Ethylene Glycol Monomethyl Ether		
Pure water	0	0.99707(7)	1.3330	1.3325
1	10.03	0.9993	1.3418	1.3412
2	20.45	1.0027	1.3511	1.3505
3	30.08	1.0055	1.3604	1.3595
4	40.09	1.0070	1.3695	1.3683
5	50.04	1.0063	1.3775	1.3762
6	60.12	1.0027	1.3847	1.3834
7	70.36	0.9955	1.3910	1.3894
8	80.04	0.9868	1.3956	1.3939
9	90.19	0.9744	1.3995	1.3977
10	99.95	0.9603	1.4021	1.4002
		Ethylene Glycol Monoethyl Ether		
Pure water	0	0.99707(7)	1.3330	1.3325
1	10.04	0.9972	1.3432	1.3425
2	20.04	0.9982	1.3539	1.3530
3	29.74	0.9983	1.3641	1.3630
4	40.05	0.9959	1.3742	1.3729
5	50.09	0.9903	1.3826	1.3812
6	59.88	0.9822	1.3898	1.3883
7	69.77	0.9718	1.3960	1.3943
8	79.81	0.9585	1.4010	1.3993
9	89.58	0.9435	1.4048	1.4031
10	99.94	0.9253	1.4077	1.4057
		Ethylene Glycol Monobutyl Ether		
Pure water	0	0.99707(7)	1.3330	1.3325
1	10.05	0.9939	1.3447	1.3440
2	20.12	0.9861	1.3552	1.3544
3	29.81	0.9774	1.3645	1.3635
4	39.81	0.9684	1.3741	1.3730
5	49.52	0.9588	1.3825	1.3812
6	59.59	0.9489	1.3917	1.3903
7	69.16	0.9391	1.3993	1.3979
8	78.86	0.9277	1.4070	1.4056
9	89.00	0.9145	1.4138	1.4122
10	99.96	0.8967	1.4193	1.4173

Table III. Smoothed Data

	Wt. %	Abs. Density G./Ml. at 25° C.	R. I., n_D At 20° C.	R. I., n_D At 25° C.
		Ethylene Glycol Monomethyl Ether		
Pure water	0	0.99707(7)	1.3330	1.3325
1	10.00	0.9993	1.3418	1.3412
2	20.00	1.0025	1.3511	1.3505
3	30.00	1.0055	1.3603	1.3594
4	40.00	1.0070	1.3694	1.3682
5	50.00	1.0063	1.3775	1.3762
6	60.00	1.0027	1.3846	1.3833
7	70.00	0.9957	1.3908	1.3892
8	80.00	0.9868	1.3956	1.3939
9	90.00	0.9745	1.3994	1.3976
10	Pure	0.9602	1.4021	1.4002
		Ethylene Glycol Monoethyl Ether		
Pure water	0	0.99707(7)	1.3330	1.3325
1	10.00	0.9972	1.3432	1.3425
2	20.00	0.9982	1.3539	1.3530
3	30.00	0.9983	1.3643	1.3632
4	40.00	0.9959	1.3742	1.3729
5	50.00	0.9903	1.3826	1.3812
6	60.00	0.9821	1.3899	1.3884
7	70.00	0.9716	1.3962	1.3945
8	80.00	0.9582	1.4011	1.3994
9	90.00	0.9428	1.4050	1.4033
10	Pure	0.9252	1.4077	1.4057
		Ethylene Glycol Monobutyl Ether		
Pure water	0	0.99707(7)	1.3330	1.3325
1	10.00	0.9939	1.3447	1.3440
2	20.00	0.9862	1.3551	1.3543
3	30.00	0.9772	1.3647	1.3637
4	40.00	0.9682	1.3743	1.3732
5	50.00	0.9584	1.3830	1.3817
6	60.00	0.9484	1.3921	1.3907
7	70.00	0.9381	1.4000	1.3986
8	80.00	0.9263	1.4078	1.4064
9	90.00	0.9130	1.4145	1.4128
10	Pure	0.8966	1.4193	1.4173

the two density curves, the change in density with composition is relatively slight; hence, analysis by density is not satisfactory. However, above 65 and 55 weight % on solutions of ethylene glycol monomethyl ether and ethylene glycol monoethyl ether respectively, density may be used in determining the glycol ether content to within ±0.1 weight % for both compounds. The curve for ethylene glycol monobutyl ether resembles the hexylene glycol-water curve (*1*). Ethylene glycol monobutyl ether above 10 weight % exhibits a steady decrease in density as the glycol ether concentration is increased and density provides a basis for analysis to within ±0.1 weight %.

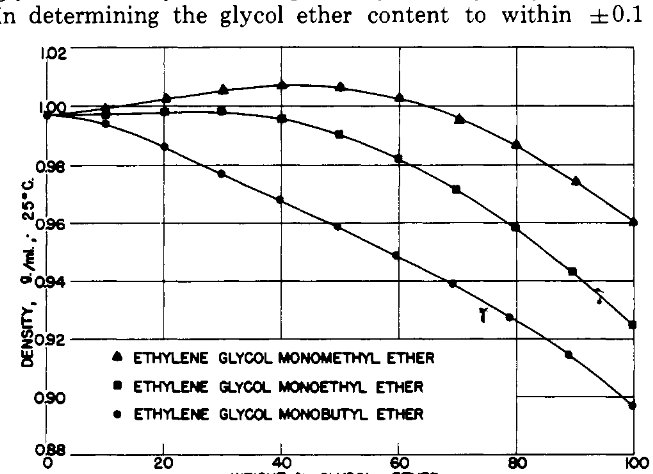

Figure 1. Density of aqueous glycol ether solutions at 25° C.

REFRACTIVE INDEX MEASUREMENTS

Refractive indices were measured with an improved precision Valentine refractometer, with compensating prism and an incandescent light source. Values were readily determined to 0.0001 (Figure 2 and Table II). By using a circulation pump connected from a constant temperature bath to the prisms of the refractometer, it was possible to main-

Table IV. Applicability of Eykman Equation

	Value of C_1 At 20° C.	Value of C_1 At 25° C.
Ethylene glycol monomethyl ether	0.5557	0.5557
Ethylene glycol monoethyl ether	0.5842	0.5843
Ethylene glycol monobutyl ether	0.6193	0.6191

Table V. Applicability of Dreisbach Equation

Compound	Density, d, G./Ml at 20° C.[a]	Density, d, G./Ml at 25° C.	Refractive Index, n_D at 20° C.	Refractive Index, n_D at 25° C.	$\Delta n/\Delta d$	Dreisbach Coefficient $(\Delta n/\Delta d) \div C_1$
Ethylene glycol monomethyl ether	0.96459	0.96024	1.4021	1.4002	0.4368	0.79
Ethylene glycol monoethyl ether	0.92945	0.92520	1.4077	1.4057	0.4706	0.81
Ethylene glycol monobutyl ether	0.90030	0.89664	1.4193	1.4173	0.5464	0.88

[a] Calculated from sp. gr. data at 20° C. listed in Table I.

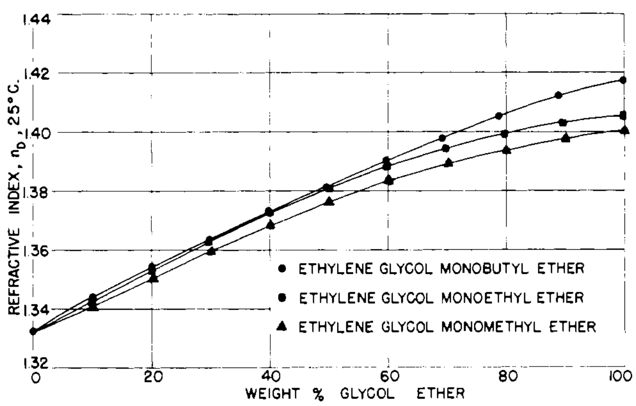

Figure 2. Refractive indices of aqueous glycol ether solutions at 25° C.

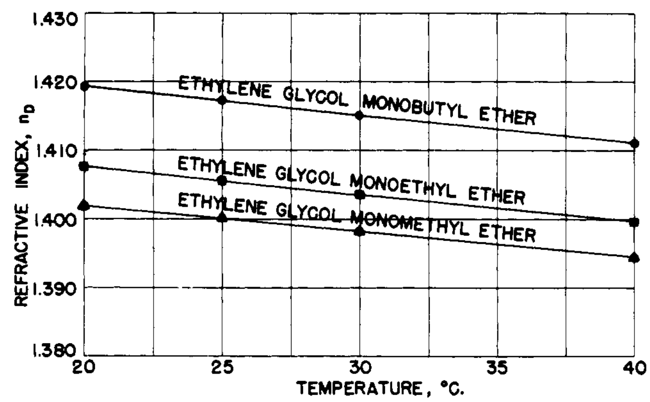

Figure 3. Effect of temperature on refractive index of pure glycol ethers.

tain the desired temperature (either 20° or 25° C.) to ±0.01° C.

For solutions of all three glycol ethers, refractive index provides an analytical method which gives the glycol ether content to within approximately ±0.15 weight % up to an ether concentration of 90%. For ethylene glycol monomethyl and monoethyl ethers above this concentration the value is approximately ±0.4%.

The effect of temperature of the refractive index of these compounds is shown in Figure 3. The values for all three 100% pure glycol ethers, obtained by extrapolating the data to zero water content, show a linear variation in refractive index with temperature over the range from 20° to 40° C.

The Eykman equation, as recommended by Kurtz, Amon, and Sankin (*6*), gave excellent checks for 20° and 25° C. for the three glycol ethers.

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

where

n = refractive index
d = density
C_1 = constant

Values of C_1 were calculated at 20° and 25° C. and are given in Table IV.

A simple empirical approximation suggested by Ward and Kurtz (*10*) for correcting the refractive index of hydrocarbons for small changes in temperature, $\Delta n = 0.6\ \Delta d$, was found not to apply to the compounds used in the present investigation. Another equation recommended by Dreisbach (*4*) for organic compounds of various Cox-chart families does not apply very well to the three ethers as shown by the deviation from the suggested coefficient of 0.8 in Table V.

$$\frac{\Delta n}{\Delta d} = 0.8\ C_1$$

where

Δn = difference in refractive index
Δd = difference in density
C_1 = constant in the Eykman equation

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