Densities and Refractive Indices of Aqueous Monoethanolamine, Diethanolamine, Triethanolamine

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Analytical data which may be used for determining compositions of aqueous solutions of monoethanolamine, diethanolamine, and triethanolamine are presented. Densities and refractive indices at 20°, 25° and 30° C. are given for binary solutions of the purified amines. Because of the point of inflection in the density-composition curve for monoethanolamine, the density data for this system are not useful for analytical purposes. Density can be used as a reasonable measure of composition for diethanolamine and triethanolamine solutions up to about 80%. Refractive index determinations provide a satisfactory analytical method over the entire composition range for all three amines.

A discussion of the advantages of plotting data of this type either *vs.* volume % or weight % is included. Values of the refractivity intercept, $[n_D - (d/2)]$, at 25° C. plotted by both methods show a nearly linear relationship for all three amines.

CONTINUING the systematic investigation of the effect of chemical structure on density and refractive index relationships (*2–4, 7*), data for aqueous solutions of monoethanolamine, diethanolamine, and triethanolamine are presented. Densities and refractive indices were measured and compounds purified using the methods of Chu and Thompson (*3*).

Refractive index and density data were determined at 20°, 25°, and 30° C. Data are available (*1, 5*) for the pure compounds but not data for aqueous solutions.

PURIFICATION AND PREPARATION

The chemicals were purified by vacuum distillation and their moisture contents determined using the Karl Fischer method. Monoethanolamine contained 0.081%, diethanolamine 0.090%, and triethanolamine 0.073% water.

Within limits of experimental measurement the purified materials gave values of density and refractive index identical to those obtained by extrapolation to 100%.

Solutions were prepared at 10 different concentrations equally distributed on a weight per cent basis.

DENSITY MEASUREMENTS

All measurements of density were made under controlled temperatures with a maximum deviation of ±0.01° C. Calibrated Weld type specific gravity bottles of 100 ml. were employed. A precision of 0.0001 gram per ml. was possible by this procedure. Experimental data for aqueous solutions of the three amines are presented in Tables I, II, and III, and Figure 1.

The density-composition relationship for monoethanolamine-water solutions exhibits a maximum at about 70 weight % at all three temperatures. This means that over a considerable range of concentration density does not correspond to a unique concentration and therefore is not a useful analytical tool for this system.

At high concentrations of diethanolamine and triethanolamine, the change in density with composition is slight, and analysis by density is not satisfactory.

REFRACTIVE INDEX MEASUREMENTS

Refractive index was measured to 0.0001 using an improved Precision Valentine refractometer with the temperature controlled within ±0.01° C. Data for the three aqueous amine systems are presented in Tables I, II, and III, and Figure 2.

VOLUME CHANGE ON MIXING

It has been pointed out by Kurtz (*6*) that there is a theoretical advantage in plotting density, refractive index, and refractivity intercept against volume % rather than

Table I. Monoethanolamine–Water Solutions

Amine Wt. %	d at 25° C. G./Ml.	Refractive Index, n_D 20° C.	25° C.	30° C.
0.00	0.9971	1.3330	1.3325	1.3320
9.90	1.0007	1.3451	1.3445	1.3439
20.25	1.0053	1.3581	1.3575	1.3568
30.43	1.0106	1.3716	1.3709	1.3700
39.53	1.0161	1.3851	1.3841	1.3830
49.35	1.0193	1.3966	1.3957	1.3946
59.37	1.0243	1.4098	1.4087	1.4074
70.04	1.0262	1.4232	1.4220	1.4205
79.62	1.0251	1.4343	1.4328	1.4313
90.19	1.0201	1.4447	1.4433	1.4416
99.92	1.0127	1.4539	1.4521	1.4503

	Density, G/Ml. 20° C.	30° C.
0.00	0.9982	0.9957
10.20	1.0021	0.9993
21.99	1.0112	1.0044
28.59	1.0125	1.0085
40.38	1.0184	1.0136
50.72	1.0241	1.0183
59.32	1.0274	1.0218
71.11	1.0297	1.0233
79.62	1.0284	1.0216
90.19	1.0241	1.0168
99.92	1.0167	1.0093

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Table II. Diethanolamine–Water Solutions

Amine Wt. %	d at 25° C. G./Ml.	Refractive Index, n_D 20° C.	25° C.	30° C.
0.00	0.9971	1.3330	1.3325	1.3320
10.18	1.0087	1.3471	1.3466	1.3459
20.15	1.0209	1.3612	1.3607	1.3599
30.10	1.0331	1.3758	1.3752	1.3743
40.25	1.0461	1.3912	1.3905	1.3896
50.44	1.0588	1.4069	1.4060	1.4051
59.36	1.0693	1.4207	1.4198	1.4187
69.08	1.0788	1.4353	1.4344	1.4331
78.57	1.0861	1.4496	1.4481	1.4466
89.31	1.0923	1.4637	1.4624	1.4611
99.91	1.0935	1.4776	1.4760	1.4746

	Density, G./Ml. 20° C.	30° C.
0.00	0.9982	0.9957
10.29	1.0099	1.0072
20.31	1.0221	1.0192
30.42	1.0354	1.0316
40.49	1.0484	1.0441
50.66	1.0604	1.0566
61.00	1.0738	1.0685
67.50	1.0821	1.0765
78.57	1.0899	1.0834
89.31	1.0941	1.0887
99.91	1.0968	1.0911

Table III. Triethanolamine–Water Solutions

Amine Wt. %	d at 25° C. G./Ml.	Refractive Index, n_D 20° C.	25° C.	30° C.
0.00	0.9971	1.3330	1.3325	1.3320
10.09	1.0123	1.3477	1.3470	1.3464
20.67	1.0296	1.3635	1.3628	1.3621
30.14	1.0445	1.3783	1.3777	1.3768
40.55	1.0617	1.3951	1.3946	1.3938
49.24	1.0758	1.4095	1.4089	1.4077
53.41	1.0823	1.4165	1.4157	1.4145
70.01	1.1054	1.4436	1.4427	1.4412
78.17	1.1138	1.4559	1.4549	1.4534
89.52	1.1205	1.4718	1.4707	1.4693
99.93	1.1217	1.4850	1.4835	1.4822

	Density, G./Ml. 20° C.	30° C.
0.00	0.9982	0.9957
10.29	1.0138	1.0113
20.38	1.0299	1.0268
30.70	1.0476	1.0439
40.53	1.0639	1.0596
49.24	1.0790	1.0734
53.41	1.0851	1.0797
71.16	1.1091	1.1032
78.17	1.1166	1.1106
89.52	1.1233	1.1175
99.93	1.1236	1.1184

weight %. In the absence of volume change on mixing, both density and refractive index are additive on a volume % basis. Therefore the deviation from linearity is significant as a measure of the effect of volume change on mixing. Values for the volume change on mixing are given in Table IV.

For practical analytical or engineering work it is more convenient to have the properties on a weight basis as most calculations are based on weight % composition rather than volume %. Of course, the really important advantage of using weight % is that for a given mixture it does not change with temperature, pressure or on mixing the components.

REFRACTIVITY INTERCEPTS

Refractivity intercepts, $n_D - (d/2)$, were calculated for 20°, 25°, and 30° C. from smoothed data at ten per cent increments and are presented in Table V along with the corresponding volume % values assuming no volume change on mixing. The correlating relation presented by Rouleau and Thompson (*7*) and suggested by Kurtz (*6*) was tested by plotting the refractivity intercept values for 25° C., in Figure 3, *vs.* both volume and weight %. It can be seen that this correlation produced a nearly linear relationship for all three amines. The deviation was slightly less on the volume basis.

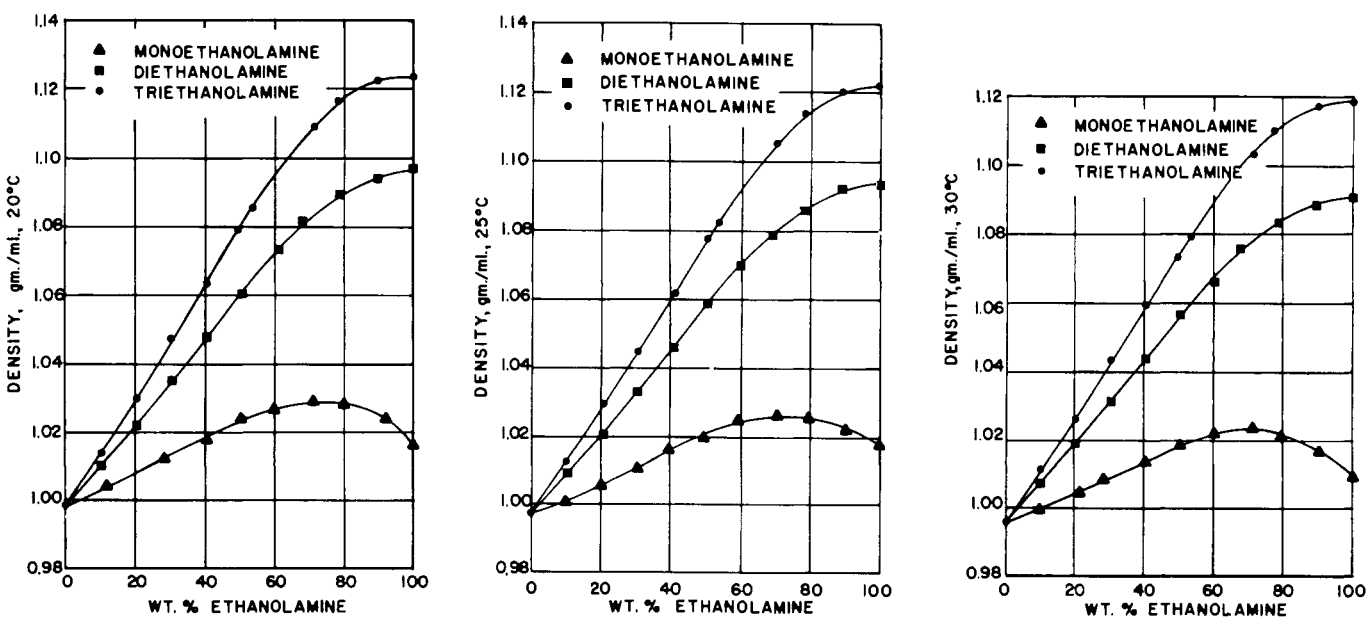

Figure 1. Densities of aqueous amine solutions: (a) 20° C.; (b) 25° C.; (c) 30° C.

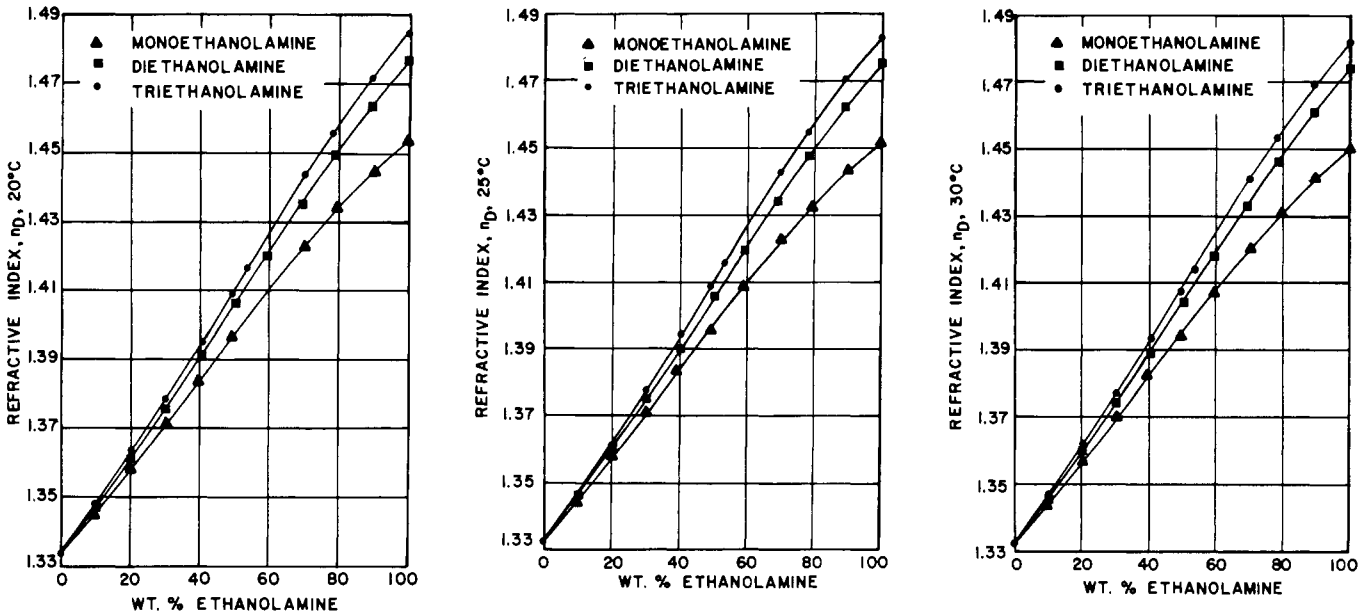

Figure 2. Refractive indices of aqueous amine solutions: (a) 20° C.; (b) 25° C.; (c) 30° C.

Table IV. Volume Change on Mixing, 25° C.

Wt. %	Volume %[a]	d, 25° C., G./Ml.	Volume Change on mixing, Ml./G.	Wt. %	Volume %[a]	d, 25° C., G./Ml.	Volume Change on mixing, Ml./G.
	Monoethanolamine–Water				Diethanolamine–Water		
0.00	0.00	0.9971	0	50.00	47.69	1.0581	0.0136
10.00	9.86	1.0007	0.0021	60.00	57.77	1.0700	0.0153
20.00	19.75	1.0053	0.0051	70.00	68.03	1.0795	0.0147
30.00	29.67	1.0103	0.0085	80.00	78.48	1.0869	0.0121
40.00	39.63	1.0157	0.0122	90.00	89.14	1.0914	0.0071
50.00	49.61	1.0207	0.0155	100.00	100.00	1.0935	0
60.00	59.63	1.0244	0.0175				
70.00	69.67	1.0261	0.0175		Triethanolamine–Water		
80.00	79.75	1.0255	0.0154	0.00	0.00	0.9971	0
90.00	89.86	1.0214	0.0100	10.00	8.99	1.0123	0.0040
100.00	100.00	1.0127	0	20.00	18.18	1.0277	0.0076
				30.00	27.59	1.0440	0.0117
	Diethanolamine–Water			40.00	37.21	1.0608	0.0157
0.00	0.00	0.9971	0	50.00	47.06	1.0771	0.0188
10.00	9.20	1.0083	0.0023	60.00	57.14	1.0921	0.0204
20.00	18.56	1.0205	0.0053	70.00	67.47	1.1049	0.0199
30.00	28.10	1.0330	0.0084	80.00	78.05	1.1145	0.0165
40.00	37.81	1.0458	0.0114	90.00	88.89	1.1204	0.0101
				100.00	100.00	1.1217	0

[a] Assuming no volume change on mixing.

Table V. Refractivity Intercepts, $n_D - d/2$

Wt. %	20° C.	25° C.	30° C.	Wt. %	20° C.	25° C.	30° C.
	Monoethanolamine–Water				Diethanolamine–Water		
0.00	0.8339	0.8340	0.8342	60.00	0.8856	0.8858	0.8861
10.00	0.8442	0.8444	0.8446	70.00	0.8959	0.8959	0.8958
20.00	0.8541	0.8544	0.8548	80.00	0.9068	0.9067	0.9066
30.00	0.8646	0.8650	0.8654	90.00	0.9177	0.9178	0.9177
40.00	0.8751	0.8754	0.8758	100.00	0.9292	0.9292	0.9291
50.00	0.8859	0.8862	0.8866				
60.00	0.8970	0.8972	0.8973		Triethanolamine–Water		
70.00	0.9082	0.9084	0.9086	0.00	0.8339	0.8340	0.8342
80.00	0.9198	0.9204	0.9207	10.00	0.8410	0.8408	0.8408
90.00	0.9319	0.9325	0.9329	20.00	0.8479	0.8479	0.8479
100.00	0.9456	0.9457	0.9457	30.00	0.8552	0.8554	0.8555
				40.00	0.8627	0.8630	0.8634
	Diethanolamine–Water			50.00	0.8707	0.8712	0.8716
0.00	0.8339	0.8340	0.8342	60.00	0.8797	0.8802	0.8807
10.00	0.8421	0.8421	0.8421	70.00	0.8894	0.8898	0.8902
20.00	0.8500	0.8501	0.8502	80.00	0.9000	0.9002	0.9004
30.00	0.8585	0.8586	0.8587	90.00	0.9108	0.9110	0.9111
40.00	0.8672	0.8673	0.8676	100.00	0.9232	0.9228	0.9230
50.00	0.8762	0.8764	0.8767				

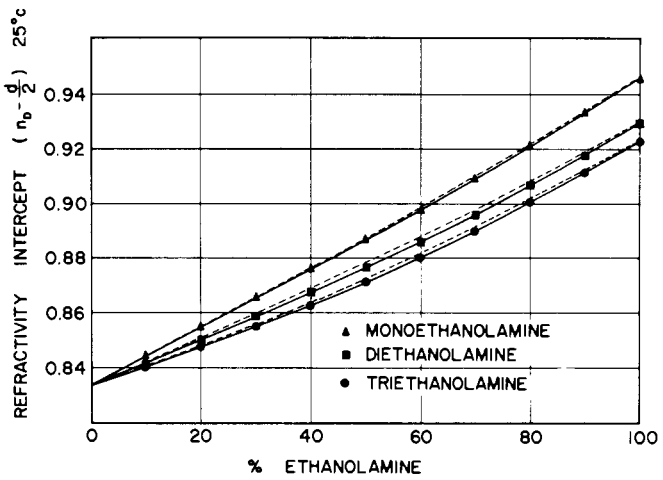

Figure 3. Refractivity intercepts for aqueous amine solutions at 25° C. Solid lines, weight %; dashed lines, volume %

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Density, Refractive Indices, Molar Refractions, and Viscosities of Diethylene Glycol Dimethyl Ether-Water Solutions at 25° C.

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Densities, refractive indices, and viscosities of mixtures of water and diethylene glycol dimethyl ether have been determined at 25°. Molar refractions are also presented. The refractive index values of the solutions increase sharply from pure water to 0.2 mole fraction ether and then slowly increase to the value for the pure ether. The partial molal volume of the ether passes through a minimum which is about 10 per cent less than the ideal molal volume at 0.03 mole fraction ether. The viscosity exhibits a pronounced maximum at 0.15 mole fraction ether. The viscosity data indicate the interaction of this ether with water is greater than that of ethylene glycol dimethyl ether while density data indicate a smaller interaction than that of the monomethyl ethers of both ethylene glycol and diethylene glycol.

DENSITIES, refractive indices, and viscosities of mixtures of diethylene glycol dimethyl ether and water have been determined at 25° as part of a study of polyether and polyether-water solvent systems. These data as well as the molar refractions of these solutions are presented.

EXPERIMENTAL

Technical diethylene glycol dimethyl ether (Ansul Chemical Company, Ansul E-141) was refluxed over metallic sodium and distilled from sodium immediately before use. The ether had a boiling point of 162° (uncorr.) and gave a negative peroxide test (2). Water used for the solutions was distilled from dilute potassium permanganate solution in a seasoned all Pyrex assembly. Methods of preparation of solutions and measurement of densities, refractive indices, and viscosities were the same as described earlier (6).

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All data are shown in Table I with solution composition being indicated as mole fraction of diethylene glycol dimethyl ether (X_2).

RESULTS AND DISCUSSION

Inspection of Table I shows that the refractive index values increase sharply to about 0.2 mole fraction ether and then increase slowly to the value of the pure ether. The molar refraction of the solutions is nearly linear with composition, with the variation being almost identical with that observed in the ethylene glycol dimethyl ether-water system, although the maximum in the refractive index of the latter is missing in the present system (6).

The density data were used to calculate the partial molal volumes by the graphical method of intercepts (3). The results of this calculation are shown in Figure 1 as the differences between the calculated partial molal volume and the ideal molal volume. These results are similar to those reported for ethylene glycol dimethyl ether-water (6)