Densities and Refractive Indices of Alcohol-Water Solutions

n-Propyl, Isopropyl, and Methyl Alcohols

KWANG-YU CHU and A. RALPH THOMPSON
Department of Chemical Engineering, University of Rhode Island, Kingston, Rhode Island

DENSITY AND REFRACTIVE INDEX DATA have been determined for aqueous solutions of methyl, *n*-propyl, and isopropyl alchohols. Procedures for purification of materials and analysis have been described by the authors in an earlier article (*4*).

Refractive index data for all three compounds were obtained at 20° and 25° C. and density data for *n*-propyl and isopropyl alcohol solutions at 25° C. Values of these properties have been reported (*1, 6, 9, 10*) for the pure alcohols (Table I) and interpolated values of data which have been given for aqueous solutions (*7*) are included for comparison (Table II). Satisfactory density data at 25° C. for aqueous solutions of methyl alcohol have been presented by Griffith (*6*) and therefore were not determined experimentally in the present work.

Table I. Properties of Pure Compounds

(Density at 25° C., G./Ml.)

Compound	Authors	Earlier Data
n-Propyl alcohol	0.7998	0.7998(*1*)
Isopropyl alcohol	0.7807	0.7808(*1*)
Methyl alcohol	0.7865	0.78654(*6*)

(Refractive Index, n_D)

	At 20° C.		At 25° C.	
Compound	Authors	Earlier Data	Authors	Earlier Data
n-Propyl alcohol	1.3854	1.3854(*9*)	1.3833	1.3833(*1*)
Isopropyl alcohol	1.3772	1.3776(*9*)	1.3749	1.3749(*1*)
Methyl alcohol	1.3287	1.3288(*9*)	1.3265	1.3277(*7*)

Table II. Experimental Data

Alcohol, Wt. %	Density, G./Ml. at 25° C. Authors	Density Earlier Data[a]	R.I. at 20° C. Authors	R.I. at 20° C. Earlier Data[a]	R.I. at 25° C. Authors	R.I. at 25° C. Earlier Data[a]	Refractivity Intercept at 25° C.
			n-Propyl Alcohol				
0	0.99707(*9, 10*)		1.3330	1.3330(*7*)	1.3325		0.8340
10.21	0.9820	0.9817(*7*)	1.3423	1.3424	1.3416		0.8506
20.27	0.9665	0.9664	1.3513	1.3506	1.3504		0.8672
29.50	0.9482	0.9481	1.3575	1.3576	1.3564		0.8823
40.18	0.9260	0.9257	1.3635	1.3637	1.3623		0.8993
49.62	0.9063	0.9060	1.3685	1.3686	1.3670		0.9139
59.76	0.8850	0.8850	1.3734	1.3733	1.3719		0.9294
69.78	0.8644	0.8644	1.3775	1.3774	1.3759		0.9437
79.74	0.8441	0.8440	1.3811	1.3809	1.3794		0.9574
89.23	0.8242	0.8242	1.3838	1.3836	1.3819		0.9698
99.94	0.7999	0.8000	1.3854	1.3850	1.3833		0.9834
			Isopropyl Alcohol				
0	0.99707(*9, 10*)		1.3330	. . . (*7*)	1.3325		0.8340
10.15	0.9806	0.9805(*7*)	1.3419	1.3393	1.3412		0.8509
19.91	0.9668	0.9673	1.3511	1.3477	1.3500		0.8666
29.73	0.9485	0.9489	1.3583	1.3541	1.3569		0.8827
39.99	0.9258	0.9267	1.3638	1.3590	1.3622		0.8993
49.36	0.9039	0.9044	1.3679	1.3629	1.3662		0.9143
60.52	0.8772	0.8776	1.3718	1.3679	1.3700		0.9314
69.24	0.8566	0.8566	1.3742	1.3709	1.3723		0.9440
77.87	0.8361	0.8359	1.3760	1.3738	1.3741		0.9561
89.84	0.8069	0.8067	1.3774	1.3769	1.3752		0.9718
99.91	0.7808	0.7815	1.3772	. . .	1.3749		0.9845
			Methyl Alcohol				
0			1.3330		1.3325	1.3323(*7*)	0.8340
10.21		0.9789(*6*)	1.3353		1.3347	1.3351	0.8453
20.19		0.9632	1.3379		1.3371	1.3378	0.8555
29.91		0.9471	1.3401		1.3391	1.3396	0.8655
39.82		0.9312	1.3417		1.3405	1.3410	0.8749
49.64		0.9130	1.3422		1.3408	1.3415	0.8843
58.89		0.8933	1.3418		1.3402	1.3412	0.8935
68.68		0.8708	1.3403		1.3385	1.3397	0.9031
79.18		0.8456	1.3375		1.3359	1.3369	0.9131
89.08		0.8196	1.3338		1.3320	1.3336	0.9222
99.94		0.7866	1.3287		1.3265	1.3279	0.9331

[a] Obtained by linear interpolation.

PREPARATION OF SOLUTIONS

The purified alcohols contained small amounts of water, as determined by means of Karl Fischer reagent. The water contents by weight were: *n*-propyl alcohol 0.06%, isopropyl alcohol 0.09%, and methyl alcohol 0.06%. The values of density and refractive index reported for 100% pure alcohols were obtained by extrapolating the data to zero water content. The data obtained for these pure alcohols were in excellent agreement with those previously reported (Table I).

Solutions were prepared, using boiled dimineralized water and the purified alcohols, at approximately 10 weight % increments to cover the entire composition range with precautions as described earlier (*4*). Compositions were known to within ±0.008%.

DENSITY MEASUREMENTS

Density measurements were made in calibrated 10-ml. Weld-type capped specific gravity bottles which were maintained at 25.00° ± 0.01° C. in a constant temperature bath. This procedure gave densities which were known to within ±0.0001 gram per ml. The experimental results for aqueous solutions of *n*-propyl and isopropyl alcohol are listed in Table II. It can be seen that there is reasonably good agreement with earlier data (*7*).

The density-composition curves (Figure 1) for both *n*-propyl and isopropyl alcohol, which nearly coincide in the range from 0 to 40 weight %, exhibit a steady decrease in density as the alcohol concentration is increased. In this respect the curves are similar to those found for hexylene glycol (*2*) ethylene glycol monobutyl ether (*4*) and diethylene glycol monobutyl ether (*3*).

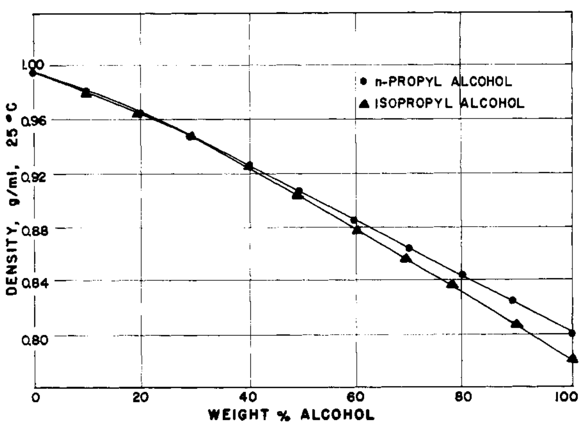

Figure 1. Densities of aqueous alcohol solutions at 25° C.

Density provides a basis for analysis to within ±0.06 weight % over the entire composition range for both *n*-propyl and isopropyl alcohols.

REFRACTIVE INDEX

Refractive indices were measured by an improved precision Valentine refractometer with compensating prism and incandescent light source. With temperature controlled (at either 20° or 25° C.) to ±0.01° C., values were readily determined to 0.0001 (Table II and Figure 2).

The older values (*7*) for refractive index of *n*-propyl alcohol solutions at 20° C. agree very well with the present data and those for methyl alcohol solutions (*7*) at 25° C. show fair agreement. Earlier data for refractive indices of isopropyl alcohol solutions at 20° C. show wide deviation from those presented here, over most of the composition range. The present data are believed to be more satisfactory due to a greater purity of the compounds and probably more precise experimental equipment.

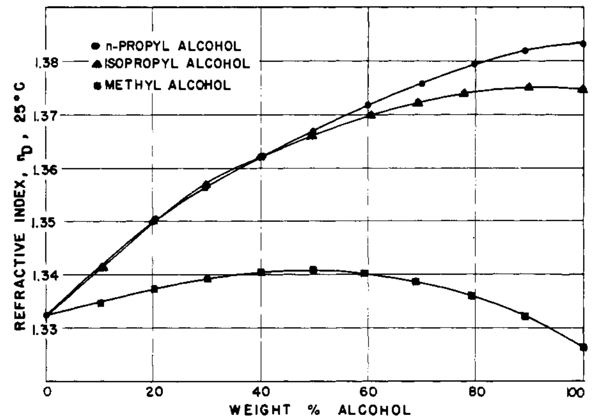

Figure 2. Refractive indices of aqueous alcohol solutions at 25° C.

For solutions of *n*-propyl and isopropyl alcohol, refractive index measurement allows determination of alcohol content to approximately ±0.20 weight % up to alcohol concentrations of 90% and 70%, respectively. Above these concentrations the values become ±0.80% and 1.25%, respectively. Because of the shallow maximum at the midpoint of the refractive index-composition curve for aqueous solutions of methyl alcohol, refractive index measurements are not useful for analytical purposes.

Effect of temperature on the refractive index of the three purified alcohols is shown in Figure 3. All three show a linear variation in refractive index with temperature over the range from 20° to 40° C.

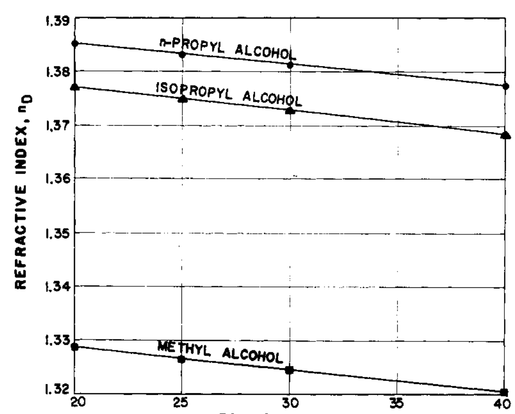

Figure 3. Effect of temperature on refractive index of pure alcohols

The Eykman equation, recommended by Dreisbach (*5*), was tested for applicability at 20° and 25° C. for the three alcohols. The 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. The equation gives excellent checks for the three alcohols at 20° and 25° C. (Table III).

REFRACTIVITY INTERCEPTS

The method of plotting refractivity intercept, $n_D - d/2$, *vs.* the composition of binary solutions, suggested by Kurtz (*8*) and presented by Rouleau and Thompson in the preceding article, was applied to the present data as plotted in Figure 4.

Once again extremely interesting correlations resulted. The lines for all three alcohols were reasonably straight; the lines for *n*-propyl alcohol and isopropyl alcohol were coincident but methyl alcohol gave a line with a different slope.

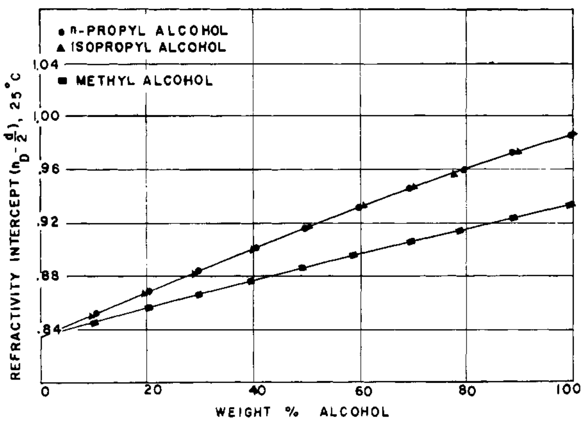

Figure 4. Refractivity intercepts for aqueous alcohol solutions at 25° C.

Table III. Applicability of Eykman Equation

Compound	Value of C_1 at 20° C.	Value of C_1 at 25° C.
n-Propyl alcohol	0.6405	0.6406
Isopropyl alcohol	0.6425	0.6424
Methyl alcohol	0.5594	0.5593

The results are very encouraging and indicate that this method of correlation might shed some light on the effect of molecular structure and association on these physical properties.

LITERATURE CITED

(1) Brunel, R.F., Crenshaw, J.L., Tobin, E., *J. Am. Chem. Soc.* **43**, 561 (1921).
(2) Chiao, T.T., Thompson, A.R., *Anal. Chem.* **29**, 1678 (1957).
(3) Chiao, T.T., Thompson, A.R., *J. Chem. Eng. Data* **6**, 192 (1961).
(4) Chu, K.Y., Thompson, A.R., J. CHEM. ENG. DATA **5**, 147 (1960).
(5) Dreisbach, R.R., *Ind. Eng. Chem.* **40**, 2269 (1948).
(6) Griffith, V.S., *J. Chem. Soc. (London)* **1954**, 860–2.
(7) "International Critical Tables," McGraw-Hill, New York, 1933.
(8) Kurtz, S.S., private communication, December 1961.
(9) Lange, N.A., "Handbook of Chemistry," 9th ed., Handbook Publ., Sandusky, Ohio, 1956.
(10) Perry, J.H., "Chemical Engineer's Handbook," 3rd ed., McGraw-Hill, New York, 1950.

RECEIVED for review September 18, 1961. Accepted February 12, 1962. Work supported by a grant from the Division of Engineering Research and Development of the University of Rhode Island.

Vapor-Liquid Equilibrium at Atmospheric Pressure for the Ternary System, Methyl Acetate–Chloroform–Benzene

ISAMU NAGATA[1]
Department of Chemical Engineering, Kyoto University, Kyoto, Japan

VAPOR-LIQUID EQUILIBRIUM data on the ternary methyl acetate–chloroform–benzene system were determined because available data indicated that this system was totally miscible and could be analyzed by density and refractive index measurements. This investigation also examined whether the experimental data can be well correlated by two typical methods existing in the literature, and whether ternary effects are present, since this system involves both positive and negative deviations from Raoult's law.

PURITY OF COMPOUNDS

First grade (Japanese industrial standards) chloroform was fractionated in a glass column packed with McMahon packings, and a heart cut was used for experimental work. First grade methyl acetate was purified by the procedure of Hurd and Strong (*8*). Special grade (Japanese industrial standards) benzene was purified by fractional crystallization repeated twice. The physical properties of the purified materials are compared with the literature values in Table I.

[1] Present address, Kanazawa University, Kanazawa, Japan

ANALYTICAL METHOD

The vapor and liquid compositions of the methyl acetate–chloroform–benzene mixtures can be easily determined by density and refractive index measurements. Uncertainty of ±0.0001 in density and refractive index means an uncertainty of 0.001 in the values of mole fraction of compositions of components.