Studies of Hemiacetal Formation in Alcohol–Aldehyde Systems. II. Refraction Studies[1]

By F. E. McKenna,[2,3] H. V. Tartar and E. C. Lingafelter

Indices of refraction have been measured for a number of alcohol–aldehyde systems; the marked positive deviations from additivity which indicate hemiacetal formation reach their maxima near 50 mole per cent. The magnitude of the deviations increases with decreasing temperature; for the reactions of a group of isomeric alcohols with a common aldehyde the deviations decrease in the order, primary > secondary > tertiary. Specific refractions in the methanol–propionaldehyde system show positive deviations from additivity at the time of mixing, but negative deviations at equilibrium.

Cryoscopic measurements[4] and infrared absorption[5] and Raman spectra[6] have given very clear proof of the existence of hemiacetals in solutions of alcohols in aldehydes. The formation of compounds between the components of a binary system will in general lead to deviations from additivity of such properties as the index of refraction. We have therefore measured the indices of refraction for a series of binary solutions of alcohols and aldehydes. Densities have also been measured in one of the systems so that specific refractions of the solutions can be calculated.

Since the completion of this work, Lauder[7] has reported indices of refraction for the systems acetaldehyde–water and acetaldehyde–methanol.

Experimental

The sources, methods of purification and physical properties of the materials used are listed in Table I.

TABLE I

Sources, Methods of Purification and Properties of Materials

Purification procedure: A, distillation at atmospheric pressure; B, distillation at reduced pressure; C, distillation in nitrogen atmosphere; D, crystallization from melt; E, treatment with Drierite at room temperature; F, treatment with potassium carbonate at room temperature; G, reflux over CaO; H, reflux over Mg.

Name	Source	Purification procedure	B.p., °C. (uncor.)
Propionaldehyde	a	C	48.0
n-Butyraldehyde	b	CECEC	74.5
iso-Butyraldehyde	a	EC	62.0
Methanol	c	A	64.6
Ethanol	d	A	78.5
1-Propanol	a	A	97.2
2-Propanol	a	HA	82.2
1-Butanol	a	A	117.7
2-Butanol	c	GAHA	99.4
2-Methyl-1-propanol	e	HA	108.0
2-Methyl-2-propanol	g	GAHA	82.6
1-Pentanol	a	A	138.0
2-Pentanol	c	GAHA	119.2
3-Pentanol	e	GAHA	116.2
3-Methyl-1-butanol	f	A	131.8

Name	Source	Purification procedure	B.p., °C. (uncor.)
3-Methyl-2-butanol	a	HA	112.4
2-Methyl-1-butanol	g	GAHA	128.6
2-Methyl-2-butanol	e	GAHA	101.9
2,2-Dimethyl-1-propanol	h	h	
1-Hexanol	a	A	157.4
1-Heptanol	a	A	176.4
1-Octanol	a	A	194.2
1-Nonanol	a	A	213.1
1-Decanol	a	A	231.3
1-Undecanol	a	DDD	M.p. 16.5
1-Dodecanol	a	B	145–146 (18 mm.)
2-Propen-1-ol	c	HA	96.9
Acetone	c	FA	56.2
Ethyl chloride	a	A	13.9–14.0
Methyl bromide	a	A	4.3–4.4
1-Butanethiol	a	EHA	97.0–97.1

[a] Eastman Kodak Co. "White Label." [b] Commercial Solvents Corp. "Butalyde." [b] C.P. anhydrous. [d] Absolute. [e] Eastman "Yellow Label." [f] J. T. Baker C.P. [g] Eastman "Blue Label." [h] This compound was prepared from 2-methyl-2-chloropropane and formaldehyde by the Grignard reaction. 2-Methyl-2-propanol was treated with concentrated hydrochloric acid at room temperature for about 30 minutes. The resulting 2-methyl-2-chloropropane was distilled off; b.p. 51°, $n^{25}D$ 1.3831. The Grignard reaction was carried out as recommended by Conant, Webb and Mendum[8] and by Adams, Noller, Gilman and Kirby.[9] The treatment with formaldehyde was continued for 2.5 hours. After hydrolysis of the Grignard addition compound, the ether layer was evaporated, yielding a greenish solid, which smelled somewhat like peppermint, but possessed a more penetrating odor. The aqueous layer was steam distilled. This yielded a little more solid. The solid was recrystallized from an ether–ethanol (1:1) solution to give a white solid. The yield was about 7% of the theoretical; m.p. 51.8°.

The indices of refraction of the methanol–propionaldehyde solutions at +0.5° and at 25° and of the ethanol–propionaldehyde solutions at 25° were determined with a Bausch and Lomb dipping refractometer, and are reported to 0.00001. The indices of refraction of all other solutions were determined with an Abbé refractometer and are reported to 0.0001. Temperature control was achieved at 25° by circulating water from a thermostated bath, at 0.5° by filling the trough of the dipping refractometer with a mixture of finely crushed ice and water, and at −64.2° by circulating acetone, cooled by Dry Ice, as recommended by Grosse.[10] The refractometers were calibrated with water at 25° and with both ethyl chloride and methyl bromide at −20 and −50°.

The densities at 25° were determined with a modified Sprengel pycnometer; those at +0.5° were determined with the dilatometer and cathetometer described by Paquette, Lingafelter and Tartar.[11] The densities at −64.2°

(1) Presented at the 106th Meeting of the American Chemical Society, New York, N. Y., September, 1944.

(2) Research Laboratories, Air Reduction Company, Inc., Murray Hill, N. J.

(3) Procter and Gamble Research Fellow, 1942–1943.

(4) F. E. McKenna, H. V. Tartar and E. C. Lingafelter, This Journal, 71, 729 (1949).

(5) A. Ashdown and T. A. Kletz, J. Chem. Soc., 1454 (1948).

(6) L. L. Neff, unpublished measurements.

(7) I. Lauder, Trans. Faraday Soc., 44, 729 (1948).

(8) J. B. Conant, C. N. Webb and W. C. Mendum, This Journal, 51, 1246 (1929).

(9) R. Adams, C. R. Noller, H. Gilman and J. E. Kirby, Org. Syntheses, 6, 22 (1926).

(10) A. V. Grosse, This Journal, 59, 2739 (1937).

(11) R. G. Paquette, E. C. Lingafelter and H. V. Tartar, ibid., 65, 686 (1943).

were determined in a pycnometer which was constructed so as to allow for contraction of the solution during thermal equilibration. The calibrated volume of the pycnometer is a U-tube which terminates in two constrictions; these constrictions are enclosed in cups provided with ground glass caps. The pycnometer was calibrated at $-64.2°$ with methanol, using the density reported by Timmermans.[12] Formation of peroxides at the low temperatures which has already been reported[13] was prevented by purging the pycnometer with nitrogen before it was filled at room temperature.

Discussion of Results

The indices of refraction for all the systems investigated are presented in Tables II–V. All of the systems exhibited positive deviations from additivity. Adkins and Broderick[14] reported that the system, 2-methyl-2-propanol and n-butyraldehyde, showed negative deviations. We have observed values which agree with theirs when measured shortly after mixing but have observed positive deviations after equilibrium was attained. This change of index of refraction with time is in agreement with the reports of Müller,[15] and of Rutovskii and Zabrodina[16] and will be discussed further in connection with the specific refractions of the methanol–propionaldehyde system.

TABLE II

DENSITIES AND REFRACTIVE INDICES OF THE METHANOL–PROPIONALDEHYDE AND ETHANOL–PROPIONALDEHYDE SYSTEMS

$N_{methanol}$	$n^{25}D$	d^{25}_4	$n^{0.5}D$	$d^{0.5}_4$
0.0000	1.36349^a	0.80350	1.37874	0.82903
.1135	1.37155	.83510	1.38440	.86590
.1643	1.37375	.84758	1.38812	.88005
.2514	1.37738	.86212	1.39210	.90272
.4042	1.38352	.88079	1.39880	.93177
.4961	1.38426	.88580	1.40162	.93952
.6147	1.37886	.87694	1.39162	.91994
.7080	1.36966	.86534	1.38050	.89831
.8155	1.35758	.84547	1.36740	.87280
.9150	1.34292	.81677	1.35222	.84259
1.0000	1.32777	.78660	1.33802	.80958

$N_{methanol}$	$n^{-64.2}D$	$d^{-64.2}_4$	$N_{ethanol}$	$n^{25}D$	d^{25}_4
0.0000	1.4144	0.90003	0.0000	1.36349^a	0.80350
.2978	1.4287	0.97400	.1705	1.37364	.82621
.5005	1.4375	1.01517	.3694	1.38136	.84643
.7524	1.4000	0.94926	.4916	1.38412	.85100
1.0000	1.3623	0.87156	.6506	1.38188	.84105
			.8071	1.37470	.82029
			.9455	1.36403	.79627
			1.0000	1.35951	.78510

^{a} $n^{25}D$ 1.36009 when the propionaldehyde is freshly distilled; after standing for a week in a sealed glass tube containing nitrogen at 25°, $n^{25}D$ 1.36349.

The maxima observed in the binary systems of propionaldehyde with the normal primary alcohols from methanol to 1-pentanol are at 50 mole per cent. For the straight-chain alcohols with more than five carbon atoms the relative indices of refraction of the pure alcohol and of the corresponding equimolar alcohol–aldehyde mixture at equilibrium (alcohol, aldehyde and hemiacetal) are such that a definite maximum is no longer obtained, al-

(12) J. Timmermans, *Sci. Proc. Roy. Dublin Soc.*, **13**, 310 (1912).

(13) F. E. McKenna, E. C. Lingafelter and H. V. Tartar, This JOURNAL, **71**, 2263 (1949).

(14) H. Adkins and A. E. Broderick, *ibid.*, **50**, 499 (1936).

(15) A. Müller, *Helv. Chim. Acta*, **17**, 1231 (1934); **19**, 225 (1936).

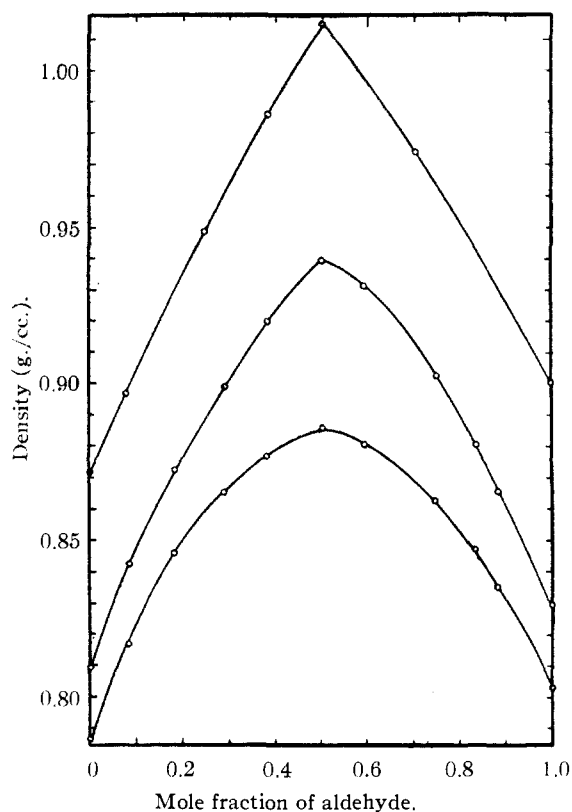(16) B. N. Rutovskii and K. S. Zabrodina, *J. Applied Chem.* (U. S. S. R.), **11**, 302 (1938).

TABLE III

REFRACTIVE INDICES OF PRIMARY ALCOHOLS WITH PROPIONALDEHYDE^a

$N_{alcohol}$	$n^{25}D$	$N_{alcohol}$	$n^{25}D$
1-Propanol		1-Butanol	
0.1737	1.3776	0.1592	1.3831
.3670	1.3893	.4038	1.3990
.4773	1.3937	.4566	1.4009
.6135	1.3935	.5491	1.4020
.8288	1.3899	.6893	1.4015
1.0000	1.3837	1.0000	1.3973
1-Pentanol		1-Hexanol	
0.0904	1.3770	0.0528	1.3732
.2034	1.3914	.2370	1.3971
.3624	1.4032	.3304	1.4076
.4259	1.4080	.4920	1.4142
.8356	1.4069	.6429	1.4153
1.0000	1.4062	1.0000	1.4150
1-Heptanol		1-Octanol	
0.0650	1.3772	0.0853	1.3858
.1667	1.3931	.3010	1.4101
.2973	1.4079	.4014	1.4160
.3789	1.4111	.5263	1.4222
.6010	1.4160	.5686	1.4235
1.0000	1.4218	.6667	1.4254
		.6735	1.4255
		1.0000	1.4274
1-Nonanol		1-Decanol	
0.1808	1.4003	0.1405	1.3989
.2723	1.4126	.3043	1.4183
.3841	1.4216	.4000	1.4242
.6593	1.4287	.7742	1.4341
1.0000	1.4318	1.0000	1.4360
1-Undecanol		1-Dodecanol	
0.1115	1.4000	0.1320	1.3871
.2211	1.4155	.3380	1.4149
.3643	1.4261	.4830	1.4277
.5567	1.4337	.8136	1.4370
1.0000	1.4380	.9189	1.4389
		1.0000	1.4396

^{a} $n^{25}D$ 1.3601 for freshly distilled propionaldehyde; $n^{25}D$ 1.3635 after standing until the alcohol–aldehyde solutions had reached equilibrium.

though a definite deviation from additivity persists. Maximum deviation in general occurs near 45 mole per cent. alcohol. The magnitude of the deviation from additivity decreases in the order, primary > secondary > tertiary alcohols.

Schimmel and Company[17] have reported that a methylene group must be adjacent to the carbonyl group so that hemiacetal formation can occur. Our results for the system, methanol–isobutyraldehyde, appear to indicate only slightly less deviation from additivity than for methanol–n-butyraldehyde.

A greater deviation from additivity is observed in the system 1-butanethiol–propionaldehyde than for 1-butanol–propionaldehyde.

Figures 1 and 2 and Table II show the density and index of refraction data used for calculation of specific refractions for the methanol–propionaldehyde system at 25, $+0.5$ and $-64.2°$. The data clearly

(17) Ann. Rept. Essent. Oils, Synthetic Perfumes, etc., Schimmel & Co., 71 (1933).

Fig. 1.—Density *versus* mole fraction of aldehyde for the system methanol–propionaldehyde: upper curve, −64.2°; middle curve, +0.5°; lower curve, +25.0°.
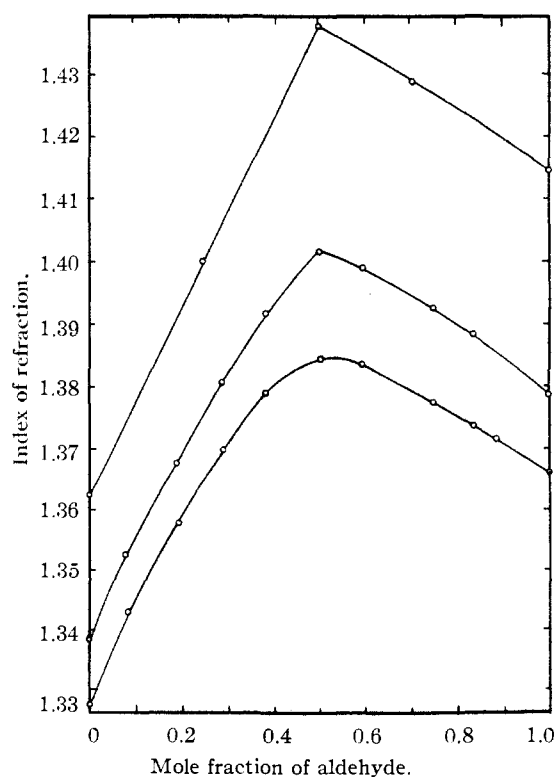

Fig. 2.—Index of refraction *versus* mole fraction of aldehyde for the system methanol–propionaldehyde: upper curve, −64.2°; middle curve, +0.5°; lower curve, +25.0°.

TABLE IV

REFRACTIVE INDICES OF ALCOHOLS WITH n-BUTYRALDEHYDE[a]

$N_{alcohol}$	$n^{25}D$	$N_{alcohol}$	$n^{25}D$
Methanol		**Ethanol**	
0.2117	1.3861	0.2892	1.3890
.4580	1.3912	.5376	1.3898
.6433	1.3822	.6547	1.3853
.7288	1.3736	.8272	1.3759
.8249	1.3603	1.0000	1.3595
1.0000	1.3278		
1-Propanol		**2-Propanol**	
0.2403	1.3908	0.2506	1.3830
.3067	1.3938	.3668	1.3835
.4890	1.3972	.6025	1.3835
.6022	1.3969	.7986	1.3816
.8042	1.3923	1.0000	1.3755
1.0000	1.3837		
2-Propen-1-ol		**1-Butanol**	
0.2582	1.3984	0.1946	1.3963
.4692	1.4072	.3845	1.4044
.6086	1.4120	.5639	1.4066
.8210	1.4122	.7967	1.4043
1.0000	1.4102	1.0000	1.3973
2-Butanol		**2-Methyl-1-propanol**	
0.1975	1.3842	0.1692	1.3930
.4227	1.3908	.3522	1.3996
.6336	1.3941	.5087	1.4023
.8095	1.3957	.7689	1.3998
1.0000	1.3950	1.0000	1.3938
2-Methyl-2-propanol		**1-Pentanol**	
0.1835	1.3832	0.2365	1.3991
.4457	1.3854	.4179	1.4085
.4748	1.3850	.5581	1.4095
.5520	1.3853	.7990	1.4083
.8342	1.3855	1.0000	1.4062
1.0000	1.3850		
3-Methyl-1-butanol		**2-Methyl-1-butanol**	
0.2386	1.3986	0.2377	1.3990
.4011	1.4074	.4212	1.4085
.5589	1.4100	.5619	1.4097
.7902	1.4096	.7986	1.4095
1.0000	1.4055	1.0000	1.4066
2,2-Dimethyl-1-propanol		**2-Pentanol**	
0.1842	1.3946	0.1636	1.3891
.3451	1.4064	.4261	1.3969
.6293[b]	1.4100	.6188	1.4019
3-Pentanol		.7996	1.4040
0.2364	1.3913	1.0000	1.4052
.4349	1.3983	**3-Methyl-2-butanol**	
.5439	1.4012	0.1928	1.3901
.8021	1.4061	.2807	1.3934
1.0000	1.4072	.5198	1.4006
2-Methyl-2-butanol		.7403	1.4040
0.2320	1.3860	1.0000	1.4076
.3791	1.3901		
.5625	1.3940		
.7984	1.4987		
1.0000	1.4018		

[a] $n^{25}D$ 1.3767 for freshly distilled n-butyraldehyde; this value was found to remain constant for the time required for these systems to attain equilibrium. [b] This is the solubility limit of the alcohol in the aldehyde at 25°.
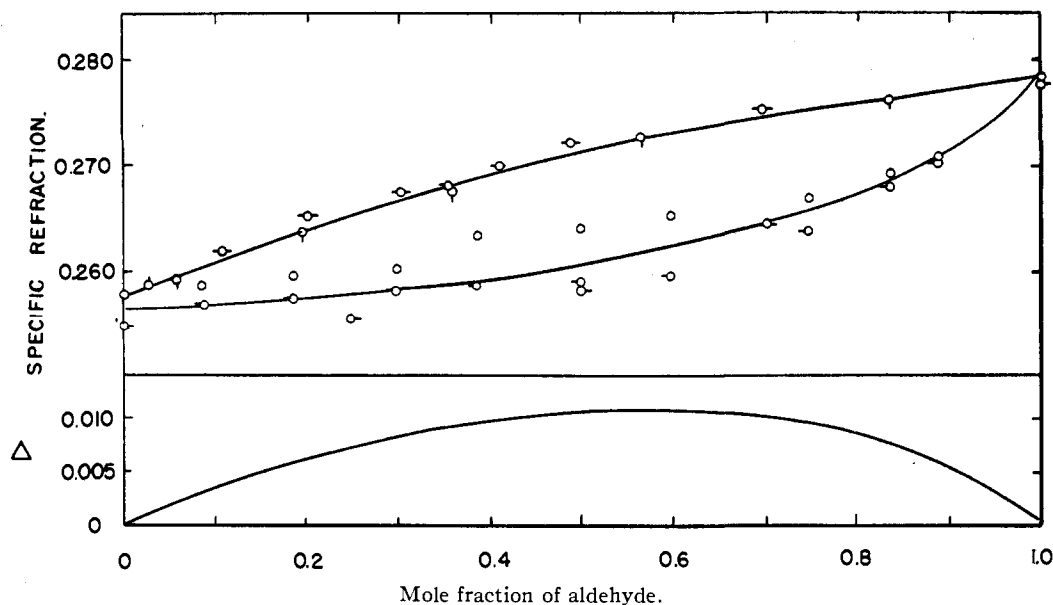
Fig. 3.—Specific refraction *versus* mole fraction of aldehyde for the system methanol–propionaldehyde: upper part, ⊙, 25°; ⊖, 0.5°; ⊙, −64.2°; ⊖, at time of mixing, 25°; ⊙, methanol–acetone at 20° (Sumarokov and Davydova[19]). Lower part, difference between equilibrium values and time of mixing values.

TABLE V
REFRACTIVE INDICES

$N_{alcohol}$	$n^{25}D$	$N_{alcohol}$	$n^{25}D$
Methanol–Isobutyraldehyde[a]		1-Butanethiol–n-Butyraldehyde	
0.3969	1.3821	0.0503	1.3780
.5128	1.3829	.3966	1.4481
.6110	1.3768	.6498	1.4540
.7516	1.3616	1.0000	1.4411
.8471	1.3491		
1.0000	1.3278		

[a] $n^{25}D$ 1.3705 for isobutyraldehyde; this value was found to remain constant for the time required for this system to attain equilibrium.

show the greater stability of the hemiacetal at the lower temperatures.

The specific refractions for the methanol–propionaldehyde system are shown in Fig. 3. Only a single curve has been drawn for the data obtained at the three temperatures, although the refraction values, in general, appear to be slightly lower at the lower temperatures. Also included in the figure are specific refractions for the methanol–propional-

dehyde system at the time of mixing (25° only)[18] and for the methanol–acetone system (data of Sumarokov and Davydova[19] at 20°). The latter two sets of data agree quite closely, as would be expected from the structural isomerism of acetone and propionaldehyde. If no reaction occurs, the refraction of the methanol–acetone and methanol–propionaldehyde systems should be identical. Figure 3 shows the difference between the specific refractions at equilibrium and at time of mixing. The maximum difference occurs at about 50 mole per cent. The coincidence of the ketone curve and the aldehyde curve at the instant of mixing and the subsequent difference between these curves at equilibrium is indicative of hemiacetal formation and, in addition, shows that the reaction is rapid but is not instantaneous.

SEATTLE, WASHINGTON

(18) To calculate specific refractions at zero time the index of refraction of each solution was measured at 20-second intervals after mixing and was extrapolated to zero time. The densities of the solutions were assumed to be additive at zero time.

(19) V. P. Sumarokov and M. I. Davydova, *J. Applied Chem.* (*U.S.S.R.*), **14**, 256 (1941).