Physical Sciences Section

Pakistan J. Sci. Ind. Res., Vol. 13, No. 4, December 1970

TEMPERATURE DERIVATIVES OF VISOCOSITY, DENSITY, AND REFRACTIVE INDEX FOR THE WATER-ETHANOL SYSTEM

Part VII.—The Temperature Derivatives of Refractive Index for Water and Very Dilute Aqueous Ethanol from 0.2% to 1.8% Ethanol

T.M. Qureshi

Physics Division, P.C.S.I.R. Laboratories, Karachi 39

Masuduz-zaman Qazi and M.M. Qurashi*

Defence Science Organization, Ministry of Defence, Government of Pakistan, Rawalpindi

(Received July 16, 1969)

The present communication gives the results of new experiments on temperature derivatives of refractive index with sodium D light for very dilute aqueous ethanol solutions from 0 to 2% ethanol, at concentration intervals of nearly 0.2% ethanol. All the measurements, including a set of experiments on pure water, have been duplicated with the Pulfrich and V-Block refractometers. While the temperatures of the minima are found to be essentially the same with the two refractometers, the amplitudes of about half the minima are 2 to 4 times larger with the Pulfrich instrument, and it is conjectured that this may be due to interfacial boundary effects.

The mean results are plotted as a synoptic concentration–temperature chart, showing the minima from 0% to 1.8% ethanol. It is found that, while the pattern is broadly the same as previously reported, the measurements at intervals of 0.2% ethanol concentration show up several time details, particularly at the very low ethanol concentrations, and provide evidence of branching of at least one minimum into two separate ones, as well as of rapid shifts in the region between 0 and 0.3% ethanol concentration.

Introduction

Following a preliminary experimental investigation of the temperature-derivative of refractive index of water, which showed[1] the probable existence of a roughly sinusoidal component with a period of 4 deg C to 6 deg C, further measurements of the temperature-derivative of refractive index, dn/dT, were reported on a series of five aqueous ethanol solutions in the range 2.5–11% ethanol by Qureshi, Haider and Qurashi[2] in Part I of the present series. All these results exhibited a sinusoidal component of dn/dT, which could be generally correlated with the corresponding jumps in flow activation energy, E_η, already reported by Ahsanullah and Qurashi[3] for aqueous solutions containing 2.5–30% ethanol by weight. Some refractometeric measurements at closer concentration intervals of nearly 0.6% on dilute ethanol in the range 0.4–6% (by wt) using both the Pulfrich refractometer (n_0=1.74) and the new V-block refractometer ($n_0 \pm 1.51$), have lately been reported in Part V of this series,[4] and the correlation with the temperatures of the jumps in E_η is fairly satisfactory above 2.8% ethanol, but certain discrepancies occur in the more dilute solutions. Figure 1 shows an enlarged plot of the concentration–temperature chart of the minima in (–dn/dT) for concentrations below 2.5% ethanol, and it is seen that there is considerable ambiguity regarding the progressive changes in temperature versus concentration for these minima below 1.2%. Also, it was noted in a recent paper[5] from this laboratory that the variations in this region do *not* always correspond with the changes in jumps of E_η.

The present communication accordingly deals more specifically with differential refractometric work on such very dilute ethanol solutions, and gives the results of new experiments on the temperature-derivative of refractive index for some aqueous ethanol solutions containing from 0.2 to 1.8% ethanol by weight, using sodium D light and concentration intervals of approximately 0.2%.

---

*Now at P.C.S.I.R. Laboratories, Peshawar.

For comparison with these results, some new measurements are also given for double-distilled water, and are compared with the earlier measurements using a cadmium lamp. In order to attain better objectivity, most of the measurements reported here have been duplicated with two different types of refractometers, each with a different observer.

Experimental Technique

The various solutions were prepared by adding calculated volumes of absolute ethanol (Analytical Grade) to 12 ml double-distilled water in a tall bottle, and shaking thoroughly. Solutions below 0.5% ethanol were prepared at double strength, and then diluted. The concentrations of the solutions were checked by measuring the specific gravity at 25°C, and also by refractive index data. The refractive index measurements were carried out in differential fashion (as described in Part V), each solution being measured with two different refractometers, namely a Pulfrich-type instrument (Bellingham and Stanley) and a Hilger V-Block instrument. The temperature in the liquid-sample cell was controlled and measured to within ±0.02°C as a rule.

For measuring the temperature-derivative of refractive index, dn/dT, the method is to keep the main settings of the instrument fixed, and to measure directly the change, $\Delta\theta'$, in the angle of emergence of the collimated beam from the prism of the instrument. In this way, by taking the means of measurements during heating and cooling, a reproducibility of the order of ±0.04 minute of arc, i.e. about 2.5 seconds of arc, is attainable in any one experiment. The value of dn/dT can be shown[1,4] to be proportional to the value of $\Delta\theta$ in minutes measured for every 2°C, the constants of proportionality being from 1.4 to 2.0, depending on the particular instrument.

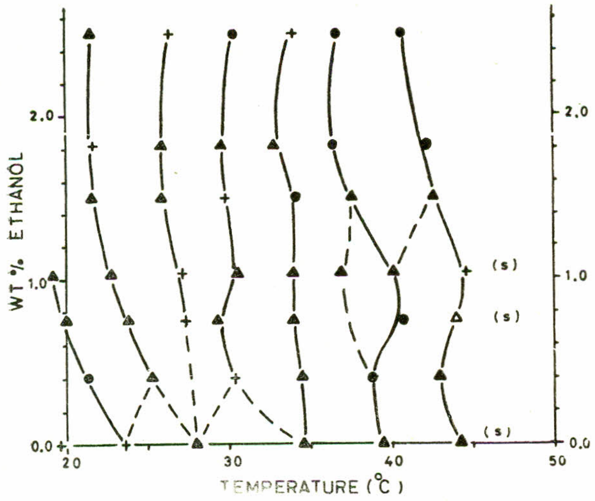

Fig. 1.—Enlarged representation of the 0% to 2.5% portion of the earlier concentration temperature chart, showing the temperatures of the minima in (−dn/dT). The crosses, triangles and circles indicate small, medium and large minima, respectively, and the letter "s" indicates that a single refractometer has been used for this particular solution.

Measurements on Solutions Containing 0.2%, 0.6% and 1.25% Ethanol

In Part V of this series, some measurements of dn/dT have already been reported for 0.41, 0.75, 1.04, 1.50 and 1.82% ethanol solutions, those for 0.75 and 1.04% being on the V-Block refracto-

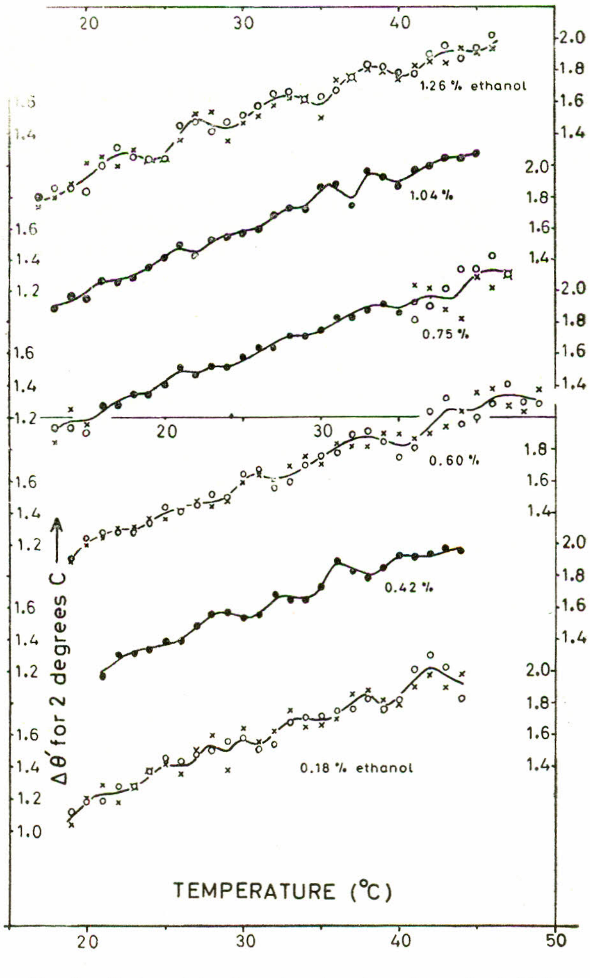

Fig. 2.—Series of six plots showing the values of -dn/dT at various temperatures for 0.2% to 1.3% ethanol solutions, obtained on the V-Block refractometer. The solid circles are the means of two sets each, previously reported for three concentrations, while the hollow circles and crosses are the results of individual experiments now performed. The r.m.s. deviation of the points about the smooth graphs is of the order of 0.02 to 0.03.

meter *alone*. The first step accordingly was to interpolate experiments with intermediate concentrations of approximately 0.2, 0.6 and 1.25% which would give us eight more or less evenly-spaced solutions up to 1.8 ethanol concentration. Tables 1 and 2 give the two sets of experimental data from 18°C to 55°C, obtained (after applying the corrections for differential evaporation) with 0.6% ethanol solution, using the V-Block refractometer. It is seen that in each table the heating and cooling values of $\Delta\theta'$ for 2 degrees C agree to within ±0.05 minutes of arc, i.e. ±3 seconds. The mean values of $\Delta\theta'$ thus obtained are plotted in the middle of Fig. 2 as hollow circles and inclined crosses, respectively, in between the graphs of the previously reported mean data on 0.4 and 0.75% ethanol, which are plotted as solid circles.

The results of similar measurements on 0.2 and 1.25% ethanol are plotted (as hollow circles and crosses) in the other graphs in Fig. 2, which also contains the graph of previously reported data for 1.04% aqueous ethanol. These six graphs show a fairly clear picture of the variations of the individual minima in $(-dn/dT)$ with changing ethanol concentration, and the positions of these minima are given in the various sections of Table 5.

Similar comparative measurements were now undertaken by another observer (T.M.Q.) on the Pulfrich instrument located in another laboratory, and the overall mean values of $-dn/dT$ for the three solutions are collected in Table 3. The overall mean values of $-dn/dT$ for the three solutions as also for 0.8% and 1.06% ethanol are plotted as circles and crosses in Fig. 3, in contrast with the solid triangles representing the mean data previously reported for the other ethanol concentrations. The positions of the various minima observed in the graphs of Fig. 3 are also given in Table 4, for comparison with the data obtained on the V-Block instrument.

Synopsis of Data from 0.2% to 1.25% Ethanol

There is good agreement between the two sets of data in Table 4, and the last two rows in each section of Table 4 give (i) the mean temperatures at the minima observed with the two instruments, together with the deviation about this mean, and (ii) the mean depths of these minima. It is at once seen that the r.m.s. deviations around these overall mean temperatures are of the order of ±0.5 to ±0.9 degree C, which is satisfactory, considering that the readings have been taken at intervals of one degree C. However, when we examine the depths of the various minima in Figs. 2 and 3, an anomaly presents itself in that, whereas some of the minima have practically identical depths in both figures, a great many of the minima in Fig. 3 have depths two to three times those of the corresponding minima in Fig. 2.

Now, the main difference between the two series of measurements on the two instruments is that the light beam passes within 30° of normal incidence in the V-Block instrument, while in the Pulfrich refractometer the beam enters at grazing incidence. It follows that in the latter case, the entering beam is somewhere between 0 and 0.2 mm of the liquid–glass interface, and the measured refractive index would therefore be several times

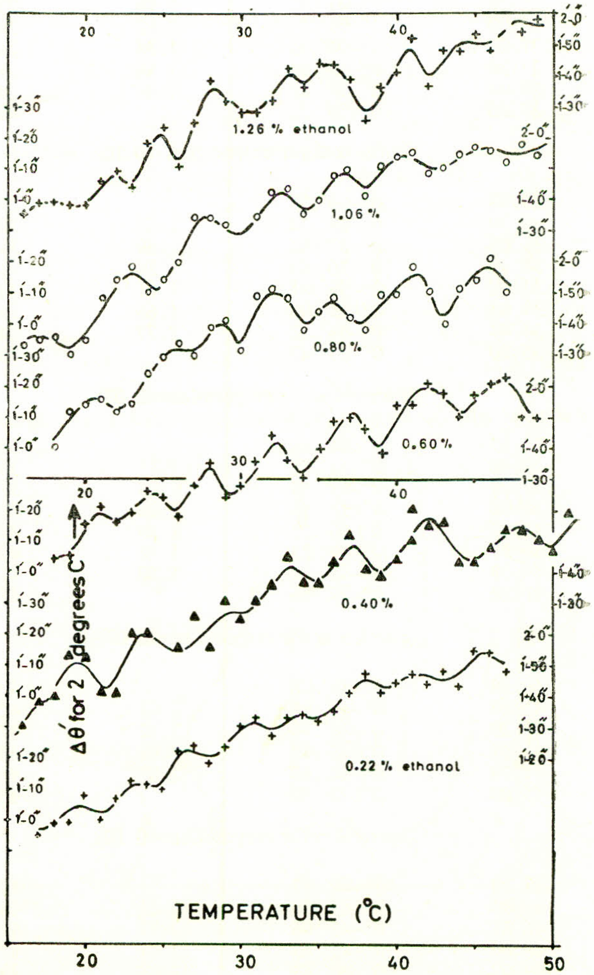

Fig. 3.—Corresponding series of plots $(-dn/dT)$ measured on the Pulfrich refractometer. The previously reported data are shown as solid triangles, while the new measurements of $(-dn/dT)$ replotted as hollow circles and crosses.

Table 1.—Differential Refractometric Measurements with 0.60 ± .02% Ethanol Solution.

First set (circles)

Temp (°C)	Heating sequence		Temp (°C)	Cooling sequence		Mean Δθ′ for heating and cooling
	Mean angle (θ′–339°)	Δθ′ for 2°C (corrected)		Mean angle (θ′–339°)	Δθ′ for 2°C (corrected)	
18.03	1°–06′.40		18.20	1°–06′.17		
19.00	1°–05′.89	1.06	19.09	1°–05′.70	1.18	1.12
20.00	1°–05′.33	1.18	20.02	1°–05′.12	1.30	1.24
21.00	1°–04′.68	1.30	21.06	1°–04′.45	1.26	1.28
21.90	1°–04′.07	1.32	22.01	1°–03′.89	1.25	1.28
23.00	1°–03′.33	1.29	23.00	1°–03′.27	1.27	1.28
23.98	1°–02′.70		23.94	1°–02′.69		
	(correction for evaporation=0.03)				(r.m.s. dev.=0.04)	
23.36	1°–03′.24		23.06	1°–03′.02		
24.34	1°–02′.56	1.34	24.00	1°–02′.44	1.35	1.34
25.20	1°–01′.92	1.46	25.00	1°–01′.81	1.42	1.44
26.08	1°–01′.21	1.42	26.09	1°–01′.06	1.38	1.41
27.00	1°–00′.55	1.38	26.98	1°–00′.53	1.52	1.45
27.80	0°–59′.94	1.40	28.20	0°–59′.56	1.65	1.52
29.00	0°–59′.05	1.46	29.00	0°–58′.96	1.54	1.50
30.00	0°–58′.22		30.08	0°–58′.26		
	(correction for evaporation=0.10)				(r.m.s. dev.=0.06)	
29.08	0°–59′.23		29.10	0°–58′.90		
30.30	0°–58′.24	1.64	30.12	0°–58′.13	1.66	1.65
31.08	0°–57′.54	1.69	31.00	0°–57 .37	1.68	1.68
31.90	0°–56′.85	1.54	31.91	0°–56′.67	1.57	1.56
33.00	0°–56′.01	1.61	33.00	0°–55′.85	1.60	1.60
34.03	0°–55′.08	1.66	34.07	0°–54′.99	1.74	1.70
34.98	0°–54′.32	1.77	34.90	0°–54′.24	1.75	1.76
35.80	0°–53′.47		35.72	0°–53′.59		
	(correction for evaporation=0.05)				(r.m.s. dev.=0.02).	
34.87	0°–54′.54		35.00	0°–53′.86		
36.00	0°–53′.51	1.75	36.18	0°–52′.91	1.80	1.78
37.08	0°–52′.53	1.88	37.00	0°–52′.13	1.91	1.90
38.00	0°–51′.56	2.00	38.01	0°–51′.22	1.84	1.92
38.82	0°–50′.73	1.89	39.12	0°–50′.25	1.81	1.85
39.87	0°–49′.73	1.76	40.00	0°–49′.49	1.74	1.75
40.99	0°–48′.74	1.80	41.00	0°–48′.68	1.82	1.81
41.98	0°–47′.76		41.88	0°–47′.82		
	(correction for evaporation=0.07)				(r.m.s. dev.=0.04)	
40.98	0°–49′.08		40.98	0°–48′.53		
42.20	0°–47′.86	2.01	42.05	0°–47′.60	2.06	2.04
43.20	0°–46′.74	2.12	42.86	0°–46′.69	2.12	2.12
44.01	0°–45 .85	2.01	43.97	0°–45′.66	1.91	1.96
44.99	0°–44′.85	2.07	45.01	0°–44′.74	1.92	2.00
45.80	0°–43′.91		45.99	0°–43′.82		
	(correction for evaporation=0.10)				(r.m.s. dev.=0.04)	
45.20	0°–44′.83		45.10	0°–44′.27		
46.00	0°–43′.90	2.22	46.00	0°–43′.52	1.96	2.09
46.81	0°–42′.96	2.17	47.34	0°–42′.18	2.25	2.21
48.00	0°–41′.63	2.01	47.85	0°–41′.53	2.20	2.10
49.02	0°–40′.63	2.08	49.06	0°–40′.37	2.10	2.09
50.20	0°–39′.24		50.39	0°–38′.99		
	(correction for evaporation=0.10)				(r.m.s. dev.=0.08)	

TABLE 2.—DIFFERENTIAL REFRACTOMETRIC MEASUREMENTS WITH 0.59+.03% ETHANOL SOLUTION.

Second set (crosses)

Temp (°C)	Heating sequence		Temp (°C)	Cooling sequence		Mean (for heating and cooling)
	Mean angle (θ′ – 339°)	Δθ for 2°C (corrected)		Mean angle (θ′ – 339°)	Δθ for 2°C (corrected)	
17.86	1°–06′.55		18.04	1°–06′.31		
19.01	1°–05′.96	1.11	19.00	1°–05′.83	1.08	1.10
20.08	1°–05′.30	1.20	20.00	1°–05′.27	1.20	1.20
21.00	1°–04′.74	1.25	20.83	1°–04′.75	1.25	1.25
22.05	1°–04′.05	1.31	21.90	1°–04′.10	1.28	1.30
23.00	1°–03′.41	1.32	23.02	1°–03′.37	1.30	1.31
23.80	1°–02′.88		24.00	1°–02′.75		
	(correction for evaporation=0.02)				(r.m.s. dev.=0.01)	
22.87	1°–03′.53		23.20	1°–03′.00		
24.00	1°–02′.76	1.31	24.02	1°–02′.45	1.41	1.36
25.00	1°–02′.08	1.31	25.01	1°–01′.77	1.40	1.36
25.98	1°–01′.41	1.43	26.00	1°–01′.11	1.42	1.42
27.00	1°–00′.60	1.48	26.99	1°–00′.41	1.46	1.47
28.02	0°–59′.85	1.45	28.02	0°–59′.69	1.43	1.44
29.07	0°–59′.05	1.49	29.00	0°–59′.03	1.48	1.48
29.98	0°–58′.34		29.93	0°–58′.32		
	(correction for evaporation=0.05)				(r.m.s. dev.=0.03)	
28.99	0°–59′.28		29.00	0°–58′.85		
30.00	0°–58′.52	1.58	30.05	0°–58′.08	1.63	1.60
31.00	0°–57′.63	1.62	31.06	0°–57′.23	1.66	1.64
31.96	0°–56′.87	1.64	32.00	0°–56′.52	1.58	1.61
32.92	0°–55′.99	1.71	33.00	0°–55′.76	1.70	1.70
34.00	0°–55′.06	1.77	34.11	0°–54′.79	1.74	1.76
34.89	0°–54′.19	1.70	35.12	0°–53′.79	1.72	1.71
35.98	0°–53′.32		36.00	0°–53′.22		
	(correction for evaporation=0.06)				(r.m.s. dev.=0.02)	
35.05	0°–54′.39		34.98	0°–54′.02		
35.91	0°–53′.54	1.81	36.00	0°–53′.10	1.88	1.84
37.20	0°–52′.38	1.79	37.00	0°–52′.18	1.84	1.82
38.08	0°–51′.53	1.77	38.17	0°–51′.17	1.86	1.82
39.20	0°–50′.55	1.91	39.04	0°–50′.34	1.90	1.90
39.96	0°–49′.69	1.99	40.19	0°–49′.31	1.81	1.90
41.06	0°–48′.64	1.86	40.98	0°–48′.64	1.88	1.87
42.00	0°–47′.73		41.96	0°–47′.70		
	(correction for evaporation=0.06)				(r.m.s. dev.=0.04)	
41.00	0°–48′.98		40.94	0°–48′.39		
42.00	0°–47′.93	1.87	42.12	0°–47′.36	1.93	1.90
42.99	0°–47′.01	1.86	42.99	0°–46′.52	2.02	1.94
44.18	0°–45′.78	2.07	44.14	0°–45′.44	2.00	2.04
45.14	0°–44′.67	2.16	45.04	0°–44′.58	2.17	2.16
46.06	0°–43′.65		46.07	0°–43′.50		
	(correction for evaporation=0.11)				(r.m.s. dev.=0.05)	
45.00	0°–44′.91		45.01	0°–44′.29		
46.00	0°–43′.79	2.24	46.00	0°–43′.34	2.12	2.18
46.80	0°–42′.79	2.10	46.80	0°–42′.48	2.06	2.08
48.00	0°–41′.59	2.02	48.20	0°–41′.19	2.07	2.04
49.00	0°–40′.46	2.14	49.07	0°–40′.24	2.23	2.18
50.00	0°- 39′.35		50.07	0°–39′.19		
	(correction for evaporation=0.10)				(r.m.s. dev.=0.04)	

more sensitive to intermolecular arrangements occurring at or near this boundary. If this is indeed the true explanation of the observed difference in amplitudes of (–d*n*/d*T*) oscillations, then a good many of the anomalies observed in (–d*n*/d*T*) must be surface-induced or at least augmented by phenomena near this boundary layer. This aspect is being studied further, and some results on pure water and the few dilute ethanol solutions have been reported separately.[6]

Data on Pure Water and Concentration–Temperature Chart for Minima of (–dn/dT).

For the purpose of the present communication, the mean depths of the minima have been estimated from Figs. 2 and 3, and these are given in the last rows of the various sections of Table 4. Using these values of depths, the various minima can be classified as small, medium, or large,

TABLE 3.—DIFFERENTIAL PULFRICH REFRACTOMETRIC DATA FOR THREE NEW DILUTE ETHANOL SOLUTIONS.

0.22% ethanol		0.60% ethanol		1.26% ethanol	
Temp (°C)	MeanΔθ for 2°C	Temp (°C)	MeanΔθ for 2°C	Temp (°C)	MeanΔθ for 2°C
16.0	—	16.0	—	16.0	0′–55″
17.0	0′–55″	17.0	—	17.0	0′–59″
18.0	0′–59″	18.0	1′– 4″	18.0	0′–59″
19.0	0′–59″	19.0	1′– 5″	19.0	0′–58″
20.0	1′–8″	20.0	1′–15″	20.0	0′–58″
21.0	1′– 0″	21.0	1′–21″	21.0	1′– 6″
22.0	1′– 7″	22.0	1′–16″	22.0	1′– 9″
23.0	1′–13″	23.0	1′–18″	23.0	1′– 4″
24.0	1′–11″	24.0	1′–26″	24.0	1′–18″
25.0	1′–10″	25.0	1′–24″	25.0	1′–23″
26.0	1′–22″	26.0	1′–17″	26.0	1′–11″
27.0	1′–24″	27.0	1′–28″	27.0	1′–25″
28.0	1′–18″	28.0	1′–35″	28.0	1′–38″
29.0	1′–23″	29.0	1′–23″	29.0	1′–32″
30.0	1′–30″	30.0	1′–27″	30.0	1′–28″
31.0	1′–33″	31.0	1′–36″	31.0	1′–28″
32.0	1′–27″	32.0	1′–44″	32.0	1′–32″
33.0	1′–33″	33.0	1′–36″	33.0	1′–43″
34.0	1′–34″	34.0	1′–31″	34.0	1′–37″
35.0	1′–32″	35.0	1′–40″	35.0	1′–44″
36.0	1′–35″	36.0	1′–49″	36.0	1′–44″
37.0	1′–41″	37.0	1′–50″	37.0	1′–39″
38.0	1′–48″	38.0	1′–47″	38.0	1′–26″
39.0	1′–41″	39.0	1′–38″	39.0	1′–37″
40.0	1′–44″	40.0	1′–54″	40.0	1′–42″
41.0	1′–47″	41.0	1′–54″	41.0	1′–52″
42.0	1′–43″	42.0	2′– 1″	42.0	1′–37″
43.0	1′–48″	43.0	1′–58″	43.0	1′–48″
44.0	1′–43″	44.0	1′–50″	44.0	1′–48″
45.0	1′–54″	45.0	1′–57″	45.0	1′–53″
46.0	1′–53″	46.0	2′– 1″	46.0	1′–48″
47.0	1′–48″	47.0	2′– 3″	47.0	—
48.0	—	48.0	1′–50″	48.0	1′–54″
49.0	—	49.0	1′–50″	49.0	1′–58″

according as the depth is less than 0.09′, from 0.09′ to 0.12′, or greater than 0.12′, respectively. These various minima have been plotted as crosses, triangles, and solid circles, respectively, on the refined concentration–temperature chart in Fig. 4.

To the data of Table 4 have also been added the earlier data for 1.50% ethanol and 1.82% ethanol solution, so that Fig. 4 shows eight sets of measurements from 0.2% ethanol to 1.8% ethanol.

TABLE 4.—SYNOPSIS OF V-BLOCK AND PULFRICH DATA FOR TEMPERATURE AND DEPTHS OF MINIMA OF $(-dn/dT)$ FOR 0.2% TO 1.3% AQUEOUS ETHANOL.

0.21%	V.B.	22.6	26.4	29.0	31.2	35.7	39.2	44	
	Pulf 17.7	21.4	24.6	28.4	32.3	35.3	39.6	43.4	47.0
	Mean (17.7)	22.0±.6	25.5±.9	28.7±.3	31.8±.6	35.5±.2	39.4±.2	43.7±.3	47.0±
	Depth	0.08′	.08′	.06′	.07′	.08′	.09′	.09′	
0.41%±.03	V.B.	20.5	25.3	30.6	34.2	38.3	41.9		
	Pulf 17.5	21.5	25.9	30.2	34.9	39.3	44.5]		
	Mean (17.5)	21.0±.5	25.6±.3	30.4±.2	34.6±.4	38.8±.5	43.2±.3		
	Depth	.14′	.10′	.07′	.12′	.14′	.12′		
0.60%. +00	V.B.	18	23.3	—	28.4	32.8	40.4	44.8	
	Pulf	18	22.3	25.9	29.6	34.0	39.0	44.3	
	Mean	18.0	22.8±.5	(26)	29.0±.6	33.4±.6	39.7±.7	44.6±.2	
	Depth		.06′	.05′	.13′	.14′	.16′	.10′	
0.78%∓.02	V.B.	20	23.8	27.3	29.3	34.1	40.1	43.5	47
	Pulf	18	22.4	27.1	29.9	34.2	37.7	43.0	48
	Mean	19.0±.0	23.1±.7	27.2±.1	29.6±.3	34.2±.6	38.9±1.2	43.2±.3	47.5±
	Depth	.09′	.10′	.04′	.11′	.09′	.18′	.10′	
1.05%±.01	V.B.	19.4	22.8	27.1	30.8	34.0	37.0	40.1	
	Pulf	19.2	24.7	—	30.0	34.4	38.0	42.7	48
	Mean	19.3±.1	23.8±.9	(27)	30.4±.4	34.2±.2	37.5±.5	41.4±1.3	(48)
	Depth	.11′	.12′	.04′	.10′	.10′	.12′	.09′	.04′
1.26%∓.01	V.B.	18.2	24±1	25±1	29.3	35.0	40.3	44.8	
	Pulf	19.8	22.9	26.0	30.8	34.0	38.2	42.3	46.8
	Mean	19.0±.8	23.4±.6	25.5±.5	30.0±.8	34.5±.5	39.2±1.0	43.6±1.2	(47)
	Depth	.06′	0.09′	.14′	.13′	.10′	.20′	.11′	

TABLE 5.—COMPARISON OF EARLIER AND NEW MEASUREMENTS ON PURE WATER.

Nature of incident light		Temperatures at minima of $(-dn/dT)$						
Cadmium green		20.8(25)	28.1	—	33.8	39.8	43.5	49
Cadmium red		18.8(24)	26.5	—	35.0	39.8	42.8	48.5
Mean		19.8(24.5)	27.3	—	34.4	39.8	43.2	48.8
Sodium "D" line	Pulfrich	20.1 —	27.6	31.2	34.2	39.4	44.0	49.8
	V-Block	21.0(25)	28.2	—	32.8	38.6	42.3	48.2
	Mean	20.6(25)	27.9	(31.2)	33.5	39.0	43.2	49.0
Mean depth		.05(.05)	*.09*	0.06	*.10*	*.11*	*.11*	*.12*

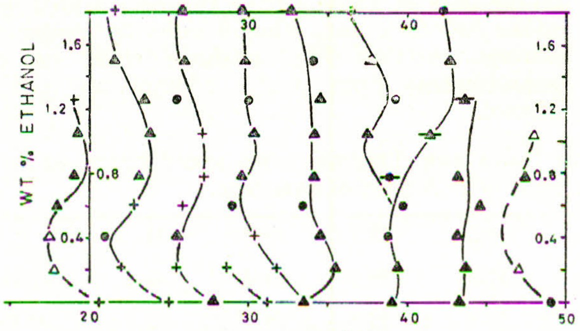

Fig. 4.—New concentration temperature chart based on the data for $(-dn/dT)$ minima in very dilute ethanol solutions from 0.2% to 1.8%, with a new set of data on pure water also included. A good deal of finer detail is observed in the lower half of this chart, in comparison with that of Fig. 1.

At this stage, it is desirable to re-examine the refractometric data obtained by Ahsanullah and Qurashi on pure water. Accordingly some new measurements have been taken using sodium D light on the Pulfrich and V-Block refractometers. The temperatures of the minima in $(-dn/dT)$ so obtained are compared in Table 5 with the earlier data of Ahsanullah and Qurashi for the cadmium green and red lines. There is essential agreement and the best mean data for use with our measurements on dilute solutions in Table 4, is given in the last two rows of Table 5, and this has accordingly been incorporated in the chart of Fig. 4.

While this chart is generally similar to that previously reported (Fig. 1) at 0.5% concentration intervals, the new data now enable us to fill in several interesting details. In the first place, the minima at 30°C and 35°C are again found to remain nearly invariant down to about 0.3% ethanol, but below this concentration these two apparently merge into the one minimum at 33.5°C. The previously ambiguous behaviour of the minima at 37° and 42°C around 1% ethanol is also now fairly well sorted out, and these two are seen to coalesce into one minimum at about 39°C below a concentration of 0.8% ethanol. Another interesting feature is that, for solutions containing less than 0.3% ethanol, there is a very rapid change in position of the minima as the concentration is varied. This suggests that a further study of the region involving small traces of ethanol in water would be interesting.

References

1. A.K.M. Ahsanullah and M.M. Qurashi, Pakistan J. Sci. Ind. Res., **6,** 243 (1963).
2. T.M. Qureshi, Z. Haider and M.M. Qurashi, Pakistan J. Sci. Ind. Res., **9,** 1(1966).
3. A.K.M. Ahsanullah and M.M. Qurashi, Proc. Roy. Soc., **285A,** 480(1965).
4. T.M. Qureshi, M. Qazi and M.M. Qurashi, Proc. Pakistan Acad. Sci., **3,** 21(1966).
5. T.M. Qurashi, M.A. Khan and M.M. Qurashi, Proc. Pakistan Acad. Sci., **5,** 81(1968).
6. M. M. Qurashi, A. K. M. Ahsanullah and Z. Sheikh, Pakistan J. Sci. Ind. Res., **12,** 324(1969–70).