

PAKISTAN JOURNAL  
OF  
SCIENTIFIC AND INDUSTRIAL RESEARCH

Vol. 9, No. 1

January 1966

**TEMPERATURE DERIVATIVES OF VISCOSITY, DENSITY AND REFRACTIVE INDEX  
FOR THE WATER—ETHANOL SYSTEM**

**Part I.—Refractometric and Flow Activation Energy Charts for Dilute Aqueous Alcohol  
from 2% to 11% Alcohol and some Concentrated Ethanol Solutions**

TAYEB M. QURESHI AND (MRS.) Z. HAIDER

*Physics Division, Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi*

AND

M.M. QURASHI

*Defence Science Organization, Ministry of Defence, Government of Pakistan, Karachi*

(Received May 18, 1965)

A systematic study of the temperature derivatives of various physical properties of the water-ethanol system is being undertaken. The three important quantities, namely viscosity, refractive index and density are first taken up, and this communication presents data on the first derivative of refractive index ( $dn/dT$ ) and viscosity ( $E_{\eta} = T^2 d \ln \eta / dT$ ) for solutions at the two ends of the system, (i) those containing 2 percent to 11 percent ethanol by weight, as well as (ii) those containing 92 percent to 95 percent ethanol by weight.

It is found that the minima of  $(-dn/dT)$  nearly coincide with the jumps in activation energy  $E_{\eta}$  for viscous flow of the dilute ethanol solutions, and a tentative chart is prepared containing a series of graphs, each showing the variation of temperature for a particular jump (and minimum of  $-dn/dT$ ) as the ethanol concentration varies from 2 percent to 11 percent by weight. A similar chart is shown for the maxima in  $(-dn/dT)$ , and some anomalies are noted.

Similar refractometric measurements are given for 92 percent to 95 percent ethanol, where certain abrupt changes had previously been observed in the cyclic variations of activation energy. The growth of an 'anomalous' maximum and minimum is followed very readily on the  $dn/dT$  curves. Further measurements on dilute and concentrated ethanol are in progress.

### Introduction

In part II of an earlier series of papers, it was found that the refractometric data on benzene<sup>1</sup> showed a definite relationship with the viscosity and dilatation, while in Part III, the measurements of  $dn/dT$  for five solutions of alcohol in water<sup>2</sup> were compared with the data for jumps in activation energy  $E_{\eta}$  for corresponding solutions, and it was found that the temperatures for these jumps correspond quite closely with those for the minima in the graphs of  $(-dn/dT)$  against temperature. The degree of this agreement is seen from Table I based on the data of the earlier papers, and the root-mean-square value of the differences between the temperatures at the jumps and the corresponding minima of  $-dn/dT$  is  $\pm 0.4^{\circ}\text{C}$ ., which is less than one-half of the smallest measuring interval used in the experiments, and about one-tenth of the mean interval between successive jumps in  $E/R$ .

This indicates a definite correspondence between the two phenomena, and at once opens up the field for further investigations, and particularly ena-

bles us to follow the changes in the temperatures of these jumps more readily than by the laborious viscosity measurements. Accordingly, the present communication presents some further measurements of  $(-dn/dT)$  for the series of aqueous alcohol solutions from 2 percent upto 11 percent and 92 percent to 95 percent ethyl alcohol by weight, at steps of nearly 1 percent alcohol. An attempt is made to use the total data so far obtained to plot charts showing the variation of the temperature of each jump with the concentration of ethyl alcohol, on the pattern of that for the maxima and minima of  $E/R$  in the case of nearly pure ethyl alcohol,<sup>3</sup> as shown in Fig. 3.

### Experimental Details

The technique for measuring the derivative of refractive index,  $dn/dT$ , has been described in previous communications,<sup>2,4</sup> and consists essentially in measuring the change every  $2^{\circ}\text{C}$ . in  $\theta$ , the angle of emergence of the light beam from the cell of a Pulfrich refractometer, containing the particular solution under investigation. This change,  $\Delta\theta$ , measured in minutes of arc is then proportional to  $(-dn/dT)$ , the constant of pro-



portionality being  $1.1 \times 10^4$ . The measurements were, as before, taken both during the heating and the cooling sequences, so as to eliminate any consistent errors of measurement. The readings taken during the heating and cooling sequences were staggered by one degree centigrade, so as to obtain finally an experimental point every degree. However, because of the very rapid evaporation of the solutions at temperatures above  $20^\circ\text{C}$ . (with consequent change in concentration of ethanol), it was found necessary to apply a correction for the change in concentration during each 2 degree interval.

are given in Table 2 and are plotted in Fig. 1(a), where the smooth graphs drawn through the experimental points exhibit the sinusoidal variations already observed in other concentrations. The solid circles and crosses show the measured values of  $\Delta\theta$  for  $2^\circ\text{C}$ . obtained during the heating and cooling sequences, respectively. The graphs marked Expt. II are for a repeated set of observations on the same sample, but with temperatures staggered by  $1^\circ\text{C}$ . in some cases. It is clear that the two experiments give maxima and minima in corresponding positions, and the hollow circles show the combined mean data for Expts. I and II.

TABLE I.—COMPARISON OF THE PREVIOUSLY OBSERVED TEMPERATURES AT THE JUMPS IN E/R AND THE CORRESPONDING MINIMA OF  $(-dn/dT)$  FOR FIVE SOLUTIONS OF ALCOHOL IN WATER IN THE RANGE OF  $15^\circ\text{C}$ . TO  $45^\circ\text{C}$ .

2.5% alcohol	{ Jump in E/R	16.0	20.4	26.2	30.0	36.2	40.1	—	—
	{ Min. of $-dn/dT$	—	20.6	26.0	30.8	36.4	40.6	44.5	—
5% alcohol	{ Jump in E/R	17.1	21.0	24.2	27.1	29.7	34.2	38.8	44.2
	{ Min. of $-dn/dT$	16.8	21.0	24.0	27.0	30.1	34.0	38.9	43.9
6.9% alcohol	{ Jump in E/R	14.0	18.4	23.2	26.0	29.8	33.4	36.9	40.3
	{ Min. of $-dn/dT$	14.0	17.4	22.2	25.6	30.0	33.0	36.7	—
7.9% $\pm 0.1\%$ alcohol	{ Jump in E/R	—	19.1	23.3	26.4	30.1	33.1	37.1	42.1
	{ Min. of $-dn/dT$	14.2	19.0	23.0	27.0	30.0	33.5	37.0	—
10.9% $\pm 0.1\%$ alcohol	{ Jump in E/R	13.7	19.1	23.0	27.0	32.0	35.2	40.8	45.8
	{ Min. of $-dn/dT$	—	18.6	23.0	27.0	32.0	35.6	40.5	—

Also, the solution was changed after every  $10^\circ\text{C}$ . or so to further minimise the magnitude of the errors due to incomplete correction for changes of concentration. The light used for the refractometer was obtained from a sodium lamp ( $\lambda = 5893 \text{ \AA}$ ) and cadmium vapour lamp ( $\lambda = 5086 \text{ \AA}$ ).

#### Measurements with 9% and 10% Ethanol and 3.6% and 5.7% Ethanol in Water

The largest gap in the concentrations given in Table I is that between 8% and 11% ethanol, and therefore the first experiments were made with 9.0% and 10.0% ethanol in water, using the light from a sodium lamp. The results of the measurements of  $\Delta\theta$  for every change of  $2^\circ\text{C}$ .

The r.m.s. scatter of the points about the mean graphs is less than 0.1 minute of arc.

Table 3 and Fig. 1(b) give the data and corresponding plots obtained with 3.6% and 5.7% ethanol solutions, and these again exhibit roughly sinusoidal variations of  $(-dn/dT)$ . Comparison with Table I indicates that the graphs for these four concentrations are in general accord with the results of earlier experiments.

#### Correlation of the Various Data into a Chart for Dilute Alcohol Solutions

The data of Table I and Fig. 1 can now be plotted together provisionally in the form of a chart, having ethanol concentration as ordinates and temperature for jumps in E/R and minima of  $(-dn/dT)$  as

TABLE 2 (a).—TEMPERATURE, MEAN READING OF DRUM  $\theta$  AND THE CALCULATED VALUE OF  $\Delta\theta$  FOR  $2^{\circ}\text{C.}$  CHANGE IN TEMPERATURE OF 10% ETHANOL SOLUTION IN THE RANGE  $19^{\circ}\text{C.}$ – $41^{\circ}\text{C.}$ , USING SODIUM YELLOW LIGHT.

Heating sequence					Cooling sequence				
Temperature ( $^{\circ}\text{C.}$ )	Mean angle $\theta$	Mean temperature ( $^{\circ}\text{C.}$ )	$\Delta\theta$ for $2^{\circ}\text{C.}$ (in minutes)	Corrected value of $\Delta\theta$ in minutes	Temperature ( $^{\circ}\text{C.}$ )	Mean angle $\theta$	Mean temperature ( $^{\circ}\text{C.}$ )	$\Delta\theta$ for $2^{\circ}\text{C.}$ (in minutes)	Corrected value of $\Delta\theta$ in minutes
19.0	$4^{\circ} 7' 5'' \pm 1''$		(Fresh Solution)		18.0	$4^{\circ} 2' 8'' \pm 1''$		(Fresh Solution)	
		20.0	$1' - 14'' \pm 1''$	$1' - 14'' - 1'' = 1'.21$	20.0	$4^{\circ} 1' 4'' \pm 2''$		$1' - 4'' \pm 2''$	$1' - 4'' + 10'' = 1'.23$
21.0	$4^{\circ} 5' 51'' \pm 1''$	22.0	$1' - 17'' \pm 2''$	$1' - 17'' - 1'' = 1'.27$	22.0	$3^{\circ} 59' 46'' \pm 1''$		$1' - 18'' \pm 2''$	$1' - 18'' + 10'' = 1'.47$
23.0	$4^{\circ} 4' 34'' \pm 2''$	24.0	$1' - 44'' \pm 2''$	$1' - 44'' - 2'' = 1'.70$	24.0	$3^{\circ} 58' 34'' \pm 2''$		$1' - 12'' \pm 2''$	$1' - 12'' + 10'' = 1'.37$
25.0	$4^{\circ} 2' 50'' \pm 1''$	26.0	$1' - 43'' \pm 1''$	$1' - 43'' - 2'' = 1'.69$	26.0	$3^{\circ} 57' 5'' \pm 2''$		$1' - 29'' \pm 3''$	$1' - 29'' + 11'' = 1'.67$
27.0	$4^{\circ} 1' 7'' \pm 1''$	28.0	$1' - 45'' \pm 1''$	$1' - 45'' - 3'' = 1'.70$	28.0	$3^{\circ} 55' 58'' \pm 2''$		$1' - 7'' \pm 3''$	$1' - 7'' + 11'' = 1'.30$
29.0	$3^{\circ} 59' 22'' \pm 1''$				30.0	$3^{\circ} 54' 6'' \pm 1''$		$1' - 52'' \pm 2''$	$1' - 52'' + 11'' = 2'.05$
29.0	$3^{\circ} 59' 36'' \pm 1''$		(Fresh Solution)					(Fresh Solution)	
27.0	$3^{\circ} 56' 57'' \pm 1''$		(Fresh Solution)		28.0	$3^{\circ} 52' 51'' \pm 2''$		(Fresh Solution)	
		28.0	$1' - 40'' \pm 1''$	$1' - 40'' - 6'' = 1'.57$	28.0	$3^{\circ} 51' 46'' \pm 1''$			
29.0	$3^{\circ} 55' 17'' \pm 1''$	30.0	$1' - 56'' \pm 2''$	$1' - 56'' - 6'' = 1'.84$	30.0	$3^{\circ} 50' 8'' \pm 2''$		$1' - 38'' \pm 2''$	$1' - 38'' + 10'' = 1'.80$
31.0	$3^{\circ} 53' 21'' \pm 2''$	32.0	$1' - 41'' \pm 2''$	$1' - 41'' - 7'' = 1'.57$	32.0	$3^{\circ} 48' 32'' \pm 1''$		$1' - 36'' \pm 2''$	$1' - 36'' + 10'' = 1'.77$
33.0	$3^{\circ} 51' 40'' \pm 1''$	34.0	$2' - 5'' \pm 2''$	$2' - 5'' - 8'' = 1'.95$	34.0	$3^{\circ} 47' 4'' \pm 1''$		$1' - 28'' \pm 1''$	$1' - 28'' + 11'' = 1'.65$
35.0	$3^{\circ} 49' 35'' \pm 2''$	36.0	$1' - 45'' \pm 3''$	$1' - 45'' - 8'' = 1'.62$	36.0	$3^{\circ} 45' 34'' \pm 0''$		$1' - 30'' \pm 1''$	$1' - 30'' + 11'' = 1'.69$
37.0	$3^{\circ} 47' 50'' \pm 2''$	38.0	$2' - 5'' \pm 3''$	$2' - 5'' - 8'' = 1'.95$	38.0	$3^{\circ} 43' 57'' \pm 1''$		$1' - 37'' \pm 1''$	$1' - 37'' + 11'' = 1'.80$
39.0	$3^{\circ} 45' 45'' \pm 2''$	40.0	$1' - 59'' \pm 2''$	$1' 59'' - 8'' = 1'.85$	40.0	$3^{\circ} 42' 12'' \pm 0''$		$1' - 45'' \pm 1''$	$1' - 45'' + 12'' = 1'.95$
41.0	$3^{\circ} 43' 46'' \pm 1''$								
39.0	$3^{\circ} 46' 28'' \pm 2''$		(Fresh Solution)						



TABLE 2 (b).—TEMPERATURES, MEAN READINGS OF DRUM  $\theta$  AND THE CALCULATED VALUES OF  $\Delta\theta$  FOR 2°C. CHANGE IN TEMPERATURE FOR 10% ETHANOL SOLUTION IN THE RANGE 18°C. TO 42°C. USING SODIUM YELLOW LIGHT.

Heating sequence					Cooling sequence				
Temperature (°C.)	Mean angle $\theta$	Mean temperature (°C.)	$\Delta\theta$ for 2°C. in minutes	Corrected value of $\Delta\theta$ in minutes	Temperature (°C.)	Mean angle $\theta$	Mean temperature (°C.)	$\Delta\theta$ for 2°C. in minutes	Corrected value of $\Delta\theta$ in minutes
18.0	3° 38' 40" ± 1		(Fresh Solution)		19.0	3°-39' 19" ± 1		(Fresh Solution)	
20.0	3° 37' 15" ± 1	19.0	1'-25" ± 1"	1'-25"-8'=1.28	19.0	3°-38' 43" ± 1	20.0	1'-6" ± 1"	1'-6" + 9"=1.25
22.0	3° 35' 45" ± 2"	21.0	1'-30" ± 2"	1'-30"-8'=1.37	21.0	3°-37' 37" ± 0	22.0	1'-10" ± 1"	1'-10" + 9"=1.31
24.0	3° 34' 25" ± 1	23.0	1'-20" ± 2"	1'-20"-8=1.20	23.0	3°-36' 27" ± 1"	24.0	1'-15" ± 1"	1'-15" + 9"=1.40
26.0	3° 32' 35" ± 2	25.0	1'-50" ± 2"	1'-50"-8=1.70	25.0	3°-35' 12" ± 1	26.0	1'-17" ± 1"	1'-17" + 9"=1.43
		27.0	1'-29" ± 2"	1'-29"-8=1.35	27.0	3°-33' 55" ± 1		(Fresh Solution)	
28.0	3° 31' 6" ± 0				27.0	3°-33' 13" ± 1	28.0	1'-19" ± 1"	1'-19" + 10"=1.50
30.0	3° 29' 6" ± 1	29.0	2'-0" ± 1"	2'-0"-9=1.85	29.0	3°-31' 54" ± 0	30.0	1'-38" ± 1"	1'-38" + 10"=1.80
30.0	3° 29' 55" ± 2		(Fresh Solution)						
32.0	3° 28' 16" ± 2	31.0	1'-39" ± 3"	1'-39"-9=1.50	31.0	3°-30' 16" ± 1	32.0	1'-24" ± 2"	1'-24" + 10"=1.57
		33.0	1'-43" ± 4"	1'-43"-9=1.57	33.0	3°-28' 52" ± 2	34.0	1'-57" ± 3"	1'-57" + 10"=2.11
34.0	3° 26' 33" ± 3"				35.0	3°-26' 55" ± 2"		(Fresh Solution)	
		35.0	1'-43" ± 4"	1'-43"-9"=1.57	35.0	3°-26' 20" ± 2"			
36.0	3° 24' 50" ± 2"	37.0	2'-1" ± 2"	2'-1"-9"=1.87	37.0	3°-24' 50" ± 2	36.0	1'-30" ± 3"	1'-30" + 10"=1.67
38.0	3° 22' 49" ± 1"						38.0	2'-0" ± 3"	2'-0" + 11"=2.19
38.0	3° 23' 25" ± 2"		(Fresh Solution.)						
40.0	3° 21' 21" ± 2"	39.0	2'-4" ± 3"	2'-4"-10"=1.90	39.0	3°-22' 50" ± 2	40.0	1'-38" ± 2"	1'-38" + 12"=1.83
42.0	3° 18' 56" ± 3"	41.0	2'-25" ± 4"	2'-25"-10"=2.25	41.0	3°-21' 12" ± 1			
42.0	3° 19' 17" ± 2"		(Fresh Solution)						

TABLE 2 (c).—MEAN TEMPERATURE AND THE CALCULATED VALUE OF  $\Delta\theta$  (MINUTES) FOR 2°C. CHANGE IN TEMPERATURE OF 9.0% ETHANOL SOLUTION USING SODIUM YELLOW LIGHT IN THE RANGE 15°-40°C.

Mean temperature in °C.	Corrected value of $\Delta\theta$ from Expt. No. I	Corrected value of $\Delta\theta$ from Expt. No. II	Mean $\Delta\theta$ (Minutes)	Mean temperature in °C.	Corrected value of $\Delta\theta$ from Expt. No. I	Corrected value of $\Delta\theta$ from Expt. No. II	Mean $\Delta\theta$ (Minutes)
17.0	1'.10	1'.06	1'.08	29.0	1'.85	1'.99	1'.92
18.0	1'.10	1'.00	1'.05	30.0	1'.93	1'.81	1'.87
19.0	1'.25	1'.10	1'.18	31.0	1'.50	1'.53	1'.52
20.0	1'.47	1'.40	1'.44	32.0	1'.50	1'.60	1'.55
21.0	1'.45	1'.30	1'.38	33.0	1'.90	2'.15	2'.02
22.0	1'.25	1'.15	1'.20	34.0	1'.83	1'.85	1'.84
23.0	1'.25	1'.26	1'.38	35.0	1'.60	1'.68	1'.64
24.0	1'.38	1'.38	1'.20	36.0	1'.83	1'.85	1'.84
25.0	1'.85	1'.93	1'.26	37.0	2'.05	2'.10	2'.07
26.0	1'.37	1'.55	1'.38	38.0	1'.79	1'.73	1'.76
27.0	1'.60	1'.61	1'.89	39.0	1'.90	—	1'.90
28.0	1'.58	1'.75	1'.46	40.0	2'.19	2'.11	2'.15
			1'.60				
			1'.66				

 TABLE 3(a).—MEAN TEMPERATURE AND THE CALCULATED VALUE OF  $\Delta\theta$  (MINUTES) FOR 2°C. CHANGE IN TEMPERATURE OF 5.7% ETHANOL SOLUTION IN THE RANGE 13°-40°C., USING SODIUM YELLOW LIGHT.

Mean temperature in °C.	Corrected value of $\Delta\theta$ (Minutes) from Expt. No. I	Corrected value of $\Delta\theta$ (Minutes) from Expt. No. II	Mean $\Delta\theta$ (Minutes)	Mean Temperature in °C.	Corrected value of $\Delta\theta$ (Minutes) from Expt. No. I	Corrected value of $\Delta\theta$ (Minutes) from Expt. No. II	Mean $\Delta\theta$ (Minutes)
13.0	0'.95	—	0.95	28.0	1'.50	1'.40	1'.45
14.0	0'.92	—	0.92	29.0	1'.60	1'.45	1'.52
15.0	—	—	—	30.0	1'.65	1'.65	1'.65
16.0	1'.03	—	1'.03	31.0	1'.55	1'.45	1'.50
17.0	1'.10	1'.00	1'.05	32.0	1'.40	1'.45	1'.42
18.0	1'.15	1'.20	1'.17	33.0	1'.60	1'.60	1'.60
19.0	1'.10	1'.30	1'.20	34.0	1'.83	1'.73	1'.78
20.0	1'.20	1'.00	1'.10	35.0	1'.75	1'.70	1'.72
21.0	1'.15	1'.00	1'.08	36.0	1'.40	1'.55	1'.48
22.0	1'.30	1'.30	1'.30	37.0	1'.65	1'.80	1'.72
23.0	1'.35	1'.40	1'.38	38.0	1'.75	1'.75	1'.75
24.0	1'.30	1'.20	1'.25	39.0	1'.70	1'.75	1'.72
25.0	1'.33	1'.34	1'.34	40.0	1'.55	1'.50	1'.52
26.0	1'.45	1'.45	1'.45				
27.0	1'.65	1'.55	1'.60				

 TABLE 3 (b).—MEAN TEMPERATURE AND THE CALCULATED VALUE OF  $\Delta\theta$  (MINUTES) FOR 2°C. CHANGE IN TEMPERATURE OF 3.6% ETHANOL SOLUTION IN THE RANGE 20°-40°C., USING SODIUM YELLOW LIGHT.

Mean temperature in °C.	Corrected value of $\Delta\theta$ (Minutes) from Expt. No. I	Corrected value of $\Delta\theta$ (Minutes) from Expt. No. II	Mean $\Delta\theta$ (Minutes)	Mean temperature in °C.	Corrected value of $\Delta\theta$ (Minutes) from Expt. No. I	Corrected value of $\Delta\theta$ (Minutes) from Expt. No. II	Mean $\Delta\theta$ (Minutes)
20.0	1'.30	1'.10	1'.20	31.0	2'.05	2'.00	2'.02
21.0	1'.40	1'.30	1'.35	32.0	2'.15	2'.10	2'.12
22.0	1'.30	1'.20	1'.25	33.0	1'.40	1'.45	1'.43
23.0	1'.05	1'.15	1'.10	34.0	1'.36	1'.33	1'.35
24.0	1'.33	1'.15	1'.24	35.0	1'.70	1'.70	1'.70
25.0	1'.30	1'.35	1'.32	36.0	1'.65	1'.65	1'.65
26.0	1'.35	1'.40	1'.37	37.0	1'.50	1'.50	1'.50
27.0	1'.50	1'.45	1'.47	38.0	1'.60	1'.65	1'.62
28.0	1'.40	1'.40	1'.40	39.0	1'.90	1'.75	1'.82
29.0	1'.20	1'.30	1'.25	40.0	1'.80	—	1'.80
30.0	1'.25	1'.35	1'.30				



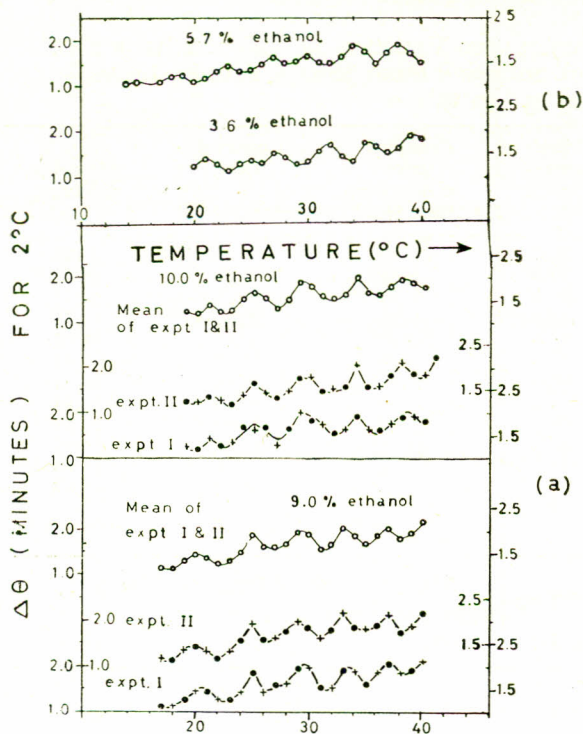


Fig. 1(a).—Plots of the experimental values of  $\Delta\theta$  (in minutes of arc) for  $2^\circ\text{C}$ ., which is equal to  $-\frac{dn}{dT} \times 1.1 \times 10^4$ , for dilute aqueous alcohol solutions containing 9.0 percent and 10.0 percent w/w ethanol. The solid circles are for the measurements during heating while the crosses are for those during the cooling sequences. The combined graph for heating and cooling is marked "Expt. I", while the ones labelled "Expt. II" are for a repeated set of observations, in which the temperatures are staggered by one degree. The uppermost graph shows the overall combined mean data for the two experiments.

1(b).—Similar plots of  $\Delta\theta$  (in minutes of arc) for  $2^\circ\text{C}$ ., obtained with 3.6 percent and 5.7 percent w/w aqueous ethanol solutions. All the four mean graphs of Figs. 1(a) and (b) exhibit a series of maxima and minima of  $(-dn/dT)$ .

abscissae. The points for contiguous concentrations can then be tentatively joined by a series of smooth lines, each of which will show the dependence of a particular energy jump on the ethanol content of the solution. Such a series of graphs is shown in Fig. 2 (a), where the hollow circles are for the temperatures obtained from the jumps in  $E/R$ , while the crosses correspond to the temperatures for the minima of  $(-dn/dT)$ . It is seen that (i) the scatter of the various points about these smooth graphs is of the order of  $\pm 0.5^\circ\text{C}$ . on the average, and (ii) the new data for  $(-dn/dT)$  for the four additional concentrations fits in well with the earlier data plotted from Table 1. However, it appears that below  $32^\circ\text{C}$ ., the crosses are about  $0.3^\circ\text{C}$ . behind the circles, while above  $32^\circ\text{C}$ ., the crosses are nearly  $0.3^\circ\text{C}$ . ahead of the circles.

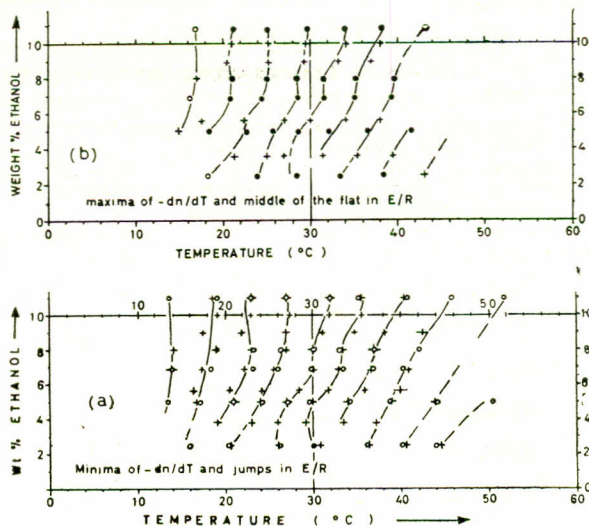


Fig. 2(a).—Tentative temperature-concentration chart<sup>s</sup> with series of graphs showing the dependence of a particular<sup>r</sup> minimum of  $-dn/dT$ , and corresponding energy jump, on the concentration of ethanol. The hollow circles are for the temperature<sup>s</sup> obtained from the jumps in  $E/R$ , and the crosses correspond to the<sup>c</sup> temperatures for the minima of  $(-dn/dT)$ . There is good overall agreement between the two sets of data, and smooth graphs are drawn showing the behaviour of each jump.

2(b).—Corresponding charts for the maxima of  $(-dn/dT)$  and the middle points of regions of constant energy. The crosses are for the maxima of  $-dn/dT$  and the solid circles are for the means of the values from  $dn/dT$  and  $E/R$  graphs. The graphs of Figs. 2(a) and (b) show anomalies at  $20^\circ\text{C}$ . and  $26^\circ\text{C}$ . for less than 4 percent ethanol solution.

The overall data now presents a fair picture of the variation of the temperature for each jump in  $E/R$  as the alcohol concentration is varied from 2.5% upto 11%. With the exception of the region between  $26^\circ$  and  $38^\circ\text{C}$ . for ethanol concentrations of 6% to 10% by weight, the individual graphs are fairly smooth. Another notable feature is that the two jumps at  $20^\circ$  and  $34^\circ\text{C}$ . for 5% ethanol solution, as also the corresponding minima and maxima of  $(-dn/dT)$  are not traceable in the 2.5% ethanol solution, thus suggesting some sort of anomalous discontinuity.

Further information is provided by the upper chart i.e. Fig. 2(b), which shows the corresponding chart for the temperatures at middle points of the flat regions of  $E/R$  and the maxima of  $(-dn/dT)$ . In this set of graphs, the temperature data for  $E/R$  and  $dn/dT$  from Table 1 are averaged and plotted as solid circles, while the new data for the maxima of  $(-dn/dT)$  for the four solutions of Tables 2 and 3 and Fig. 1 are plotted as crosses. All these data taken together provide another set of fairly smooth graphs. Of course, measurements at intermediate concentrations may alter some of the graphs.



### Some Refractometric Measurements on Concentrated Ethanol

In an earlier paper,<sup>3</sup> a somewhat similar chart had been prepared for concentrated ethanol solutions, containing 4% to 14% w/w of water, and Fig. 3(a) is a reproduction of this chart for the temperatures of the various minima observed in the activation energy,  $E_\eta$ . In view of the remarkably good correlation obtained between the variations of  $E_\eta$  and the refractometric data for dilute aqueous ethanol, it was considered worthwhile to undertake similar measurements on some concentrated ethanol solutions. The range of 92% to 95% ethanol was selected for initial study, because a somewhat anomalous behaviour is apparent for this region in the graphs of Fig. 3.

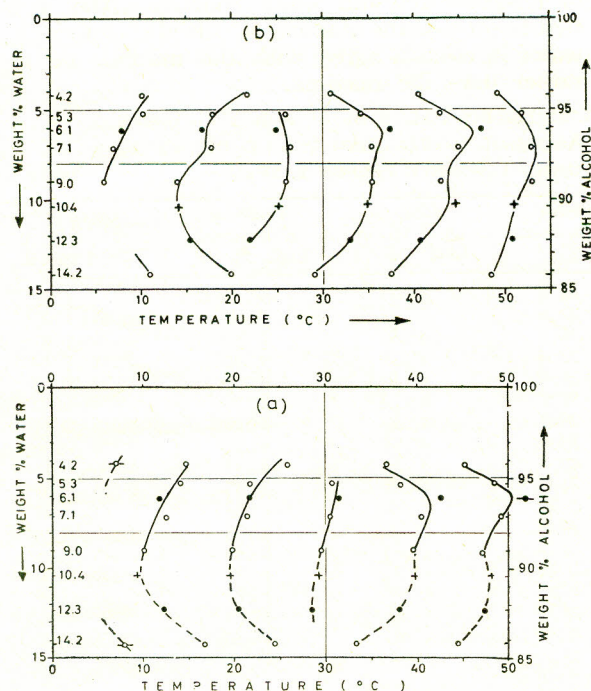


Fig. 3(a).—Temperature versus weight percent water chart for several minima of  $E_\eta$  in concentrated ethanol, from 4.2 percent to 14.2 percent w/w water in ethanol, as previously reported by Qureshi, Husain and Qurashi.

3(b).—Corresponding chart for the maxima observed with the above aqueous ethanol solutions. It appears that there are discontinuities in the neighbourhood of 5 percent and 13 percent water content.

Accordingly, a set of measurements was first made using the green line ( $\lambda = 5086 \text{ \AA}$ ) from a cadmium vapour lamp, with ethanol containing 7% water by weight. The values of the change in angle,  $\Delta\theta$ , for intervals of  $2^\circ\text{C}$ . are plotted in the lowest pair of graphs of Fig. 4(a), the crosses

being for heating and the triangles for cooling. The concentration of the solution was checked with the help of its viscosity and refractive index at  $20^\circ\text{C}$ . and  $25^\circ\text{C}$ ., both before and after each

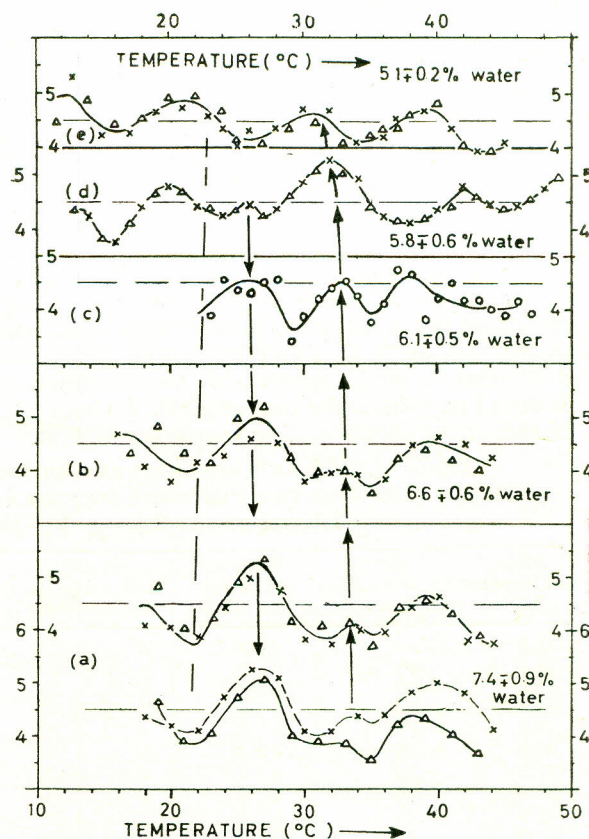


Fig. 4.—Plots of  $\Delta\theta$  (in minutes) for  $2^\circ\text{C}$ ., which equals  $-dn/dT \times 1.1 \times 10^4$ , for five concentrated aqueous ethanol solutions containing 5 percent to 8 percent water by weight. The lowest pair of graphs in Fig. 4(a) show the data obtained with a solution containing  $7.4 \pm 0.9$  percent water, the crosses being for the heating sequence, and the triangles for the cooling sequence. The consistent difference between the two is due to the progressive loss of ethanol by evaporation, and the upper graph in Fig. 4(a) shows the combined plot after application of the corresponding correction.

Fig. 4(b) and (c) show the results of similar measurements on solutions containing 6.6 percent and 6.1 percent water on the average. The incipient maximum and minimum observable in Fig. 4(a) at  $33^\circ\text{C}$ . and  $35^\circ\text{C}$ ., respectively, are now seen to increase in prominence as the water content of the solution is decreased.

Figs. 4(d) and (e) show the corresponding graphs obtained for solutions containing 5.8 percent and 5.1 percent water, wherein the large maximum at  $26^\circ\text{C}$ . is seen to diminish and disappear. The two successions of arrows going up and down the height of the whole figure show the directions of growth of this maximum and that at  $32^\circ\text{C} \pm 1^\circ\text{C}$ .

experiment, and it was found that during any one sequence (heating or cooling), the water content changed from  $6.5\% \pm 0.1\%$  upto  $8.3\% \pm 0.1\%$ ,



giving a mean of  $7.4\% \pm 0.9\%$  water. This increase in water content could be attributed to the relatively rapid progressive evaporation of the ethanol during the experiment. There is seen to be a corresponding, more-or-less consistent, difference of about 0.5 minutes of arc below  $30^\circ\text{C}$ . between the graphs through the crosses and the triangles, and about 0.6 minutes of arc from  $30^\circ$  to  $45^\circ\text{C}$ . Accordingly, half of these quantities can be applied as a correction (with opposite signs) to the two sets of readings. The combined corrected values are plotted as the upper graph in Fig. 4(a), where the r.m.s. deviation of the individual points about this graph is seen to be about 0.2 minutes of arc. This combined graph shows two distinct maxima at  $26^\circ\text{C}$ . and  $39^\circ\text{C}$ . (rising about  $0.8 \pm 0.2$  minute of arc above the mean), while the intermediate minimum has a further incipient max. and min. superposed on it at about  $33^\circ\text{C}$ . and  $35^\circ\text{C}$ . The maximum at  $26^\circ\text{C}$ . agrees with the maximum of E/R in Fig. 3(b), while that at  $39^\circ\text{C}$ . is about  $2^\circ\text{C}$ . ahead of the corresponding maximum in E/R.

the data for 5.8% water (Table 4) being the means of two experiments. These last two graphs confirm the trends noted above, and the two successions of arrows going up and down the height of Fig. 4 show the directions of growth of the maxima at  $32^\circ\text{C} \pm 1^\circ\text{C}$ . and  $26^\circ\text{C}$ ., respectively. In particular, the maximum at  $26^\circ\text{C}$ . and associated minimum at  $28^\circ\text{C}$ . are barely observable with 5.8% water, and are absent from the graph for ethanol containing 5.1% water. This agrees with the earlier finding of Qureshi, Hussain and Qurashi, that the maximum and minimum observed in activation energy  $E_\eta$  at  $26^\circ\text{C}$ . and  $30^\circ\text{C}$ ., respectively, disappeared suddenly when the water concentration was changed from 5.3% to 4.2%. Thus, the refractometric observations confirm the occurrence of a significant structural change inside the liquid in the above-mentioned ranges of temperatures and water content. Also, it is significant that the maxima of  $(-dn/dT)$  for 5.1% water in ethanol agree with the minima of  $E_\eta$  rather than the maxima.

TABLE 4.—MEAN TEMPERATURE AND THE CALCULATED VALUE OF  $\Delta\theta$  FOR  $2^\circ\text{C}$ . CHANGE IN TEMPERATURE FOR CONCENTRATED ALCOHOL CONTAINING  $5.8 \pm 0.6\%$  WATER IN THE RANGE  $13^\circ\text{--}49^\circ\text{C}$ . USING CADMIUM GREEN LINE.

Mean temperature $^\circ\text{C}$ .	Value of $\Delta\theta$ from Expt. No. I	Value of $\Delta\theta$ from Expt. No. II	Overall mean of Expt. No. I and II	Mean temperature $^\circ\text{C}$ .	Value of $\Delta\theta$ from Expt. No. I	Value of $\Delta\theta$ from Expt. No. II	Overall mean of Expt. No. I and II
13.0	4'.22	4'.46	4'.34 $\pm$ 0.22'	32.0	5'.00	5'.36	5'.32 $\pm$ 0.32'
14.0	4'.32	4'.25	4'.28 $\pm$ 0.03'	33.0	5'.25	4'.82	5'.04 $\pm$ 0.22'
15.0	3'.80	3'.83	3'.81 $\pm$ 0.02'	34.0	4'.86	5'.00	4'.93 $\pm$ 0.07'
16.0	3'.70	3'.85	3'.78 $\pm$ 0.07'	35.0	4'.25	4'.50	4'.38 $\pm$ 0.12'
17.0	4'.00	4'.25	4'.12 $\pm$ 0.13'	36.0	4'.40	4'.04	4'.22 $\pm$ 0.18'
18.0	4'.65	4'.17	4'.41 $\pm$ 0.24'	37.0	4'.10	4'.25	4'.18 $\pm$ 0.07'
19.0	4'.80	4'.56	4'.68 $\pm$ 0.02'	38.0	4'.30	4'.20	4'.16 $\pm$ 0.14'
20.0	4'.70	4'.95	4'.82 $\pm$ 0.13'	39.0	4'.10	4'.10	4'.10 $\pm$ 0.00'
21.0	4'.43	4'.97	4'.70 $\pm$ 0.27'	40.0	4'.25	4'.47	4'.36 $\pm$ 0.11'
22.0	4'.15	4'.75	4'.45 $\pm$ 0.22'	41.0	4'.35	4'.45	4'.40 $\pm$ 0.05'
23.0	4'.50	4'.25	4'.38 $\pm$ 0.13'	42.0	4'.90	4'.75	4'.82 $\pm$ 0.07'
24.0	4'.40	4'.13	4'.26 $\pm$ 0.13'	43.0	4'.70	4'.50	4'.60 $\pm$ 0.10'
25.0	4'.25	4'.45	4'.35 $\pm$ 0.10'	44.0	4'.30	4'.60	4'.45 $\pm$ 0.15'
26.0	4'.30	4'.38	4'.34 $\pm$ 0.04'	45.0	4'.50	4'.25	4'.38 $\pm$ 0.07'
27.0	4'.40	4'.13	4'.26 $\pm$ 0.13'	46.0	4'.55	4'.25	4'.40 $\pm$ 0.15'
28.0	4'.20	4'.53	4'.36 $\pm$ 0.17'	47.0	4'.45	4'.65	4'.55 $\pm$ 0.10'
29.0	4'.35	4'.88	4'.61 $\pm$ 0.17'	48.0	4'.80	4'.70	4'.75 $\pm$ 0.05'
30.0	4'.95	4'.75	4'.85 $\pm$ 0.10'	49.0	—	4'.95	4'.95
31.0	4'.95	5'.15	5'.05 $\pm$ 0.10'				

In order to investigate these unexpected findings, further measurements of  $dn/dT$  were carried out on ethanol containing (on the average) 6.6% and 6.1% of water by weight. The results of these are plotted in Fig. 4(b) and (c), wherein the incipient maximum and minimum (at  $33^\circ\text{C}$ . and  $35^\circ\text{C}$ ., respectively) are seen to grow more pronounced as the water percentage in the ethanol decreases. The two main maxima (at  $26^\circ\text{C}$ . and  $39^\circ\text{C}$ .), on the other hand, continue in place as before, but with progressively diminishing heights. Finally Fig. 4(d) and (e) show the graphs of  $(-dn/dT)$  obtained by careful measurements with solutions containing 5.8% water and 5.1% water,

Further experiments are being undertaken to obtain a more complete correlation between the activation energy data and that from  $dn/dT$ .

#### References

1. A. K. M. Ahsanullah, Tayeb M. Qureshi and M. M. Qurashi, Pak. J. Sci. Ind. Res., **8**, 11 (1965).
2. Z. Haider and M.M. Qurashi, Pakistan J. Sci. Ind. Res., **8**, 103 (1965).
3. Tayeb M. Qureshi, K. Hussain and M.M. Qurashi, Proc. Pakistan Acad. Sci., **2**, 21 (1965).
4. A.K.M. Ahsanullah and M.M. Qurashi, Pakistan J. Sci. Ind. Res., **6**, 243 (1963).