

# COMPARATIVE MEASUREMENTS OF THE TEMPERATURE DERIVATIVES OF VISCOSITY, DENSITY AND REFRACTIVE INDEX OF PURE LIQUIDS AND SOLUTIONS

## Part III.—Preliminary Investigation of the Temperature Derivative of Refractive Index of Dilute Aqueous Alcohol

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In previous work on pure water and pure ethylene glycol there was some evidence of correlation between  $E_\eta$ ,  $\frac{\partial n}{\partial T}$  and  $\beta$ , the coefficient of dilatation. In order to explore the interrelationship between these properties and their physical basis, it was desirable to study  $\frac{\partial n}{\partial T}$ , the temperature variation of refractive index, for dilute solutions of aqueous ethyl alcohol, for which data on activation energy is already available. Differential measurements— $\frac{\partial n}{\partial T}$ —have been made with the help of a Pulfrich refractometer for five different concentrations of dilute aqueous ethyl alcohol, using sodium yellow light. The  $\frac{\partial n}{\partial T}$  curves obtained for these solutions are almost sinusoidal. These, when compared with the activation energy curves of solutions of similar concentration, show, that the minima of  $\frac{\partial n}{\partial T}$  curves are very nearly coincident with the jumps in the corresponding  $E_\eta$  curves.

### Introduction

For some time past, the derivatives of viscosity, density and refractive index of water and other liquids and solutions have been under study in these Laboratories. In previous communications<sup>1,2</sup> a definite periodicity was observed for  $\frac{\partial n}{\partial T}$ ,

and jumps were found in the dilatation  $\frac{\partial \rho}{\partial T}$ . In part I of the present series<sup>3</sup> definite sinusoidal undulations were found in the curves for temperature variation of coefficient of dilatation i.e.  $\frac{1}{\rho} \frac{\partial \rho}{\partial T}$  for ethylene glycol.<sup>3</sup> There was some evidence for correlation between  $E_\eta$ ,  $\frac{\partial n}{\partial T}$  and  $\beta$ , the

coefficient of dilatation, in the case of pure water and pure benzene, which was studied in part II of the present series.<sup>4</sup>

In order to explore the inter-relationships between these properties and their physical basis, it was thought worthwhile to carry out similar measurements on dilute aqueous alcohol, for which measurements of  $E_\eta$  over a series of temperatures and concentrations are already available.<sup>5,6</sup> Some preliminary measurements of  $\frac{\partial n}{\partial T}$

for five solutions from 2.5 percent to 11 percent, differing in steps of 2 to 3 percent alcohol content, are presented in this brief report.

### Experimental Details

The experimental arrangements and other details are the same as in the previously reported investigation on pure water, made with a critical-incidence Pulfrich refractometer. This is made reliable to better than 0.000,01 for differential measurements, by permanently locking the tangent drum to the main divided circle. In the present case, the test solutions were usually changed at every ten to twelve degrees centigrade in order to avoid errors from concentration changes by loss of alcohol through evaporation. Pure conductivity water was used in the preparation of solutions (% given by weight), and the concentrations were verified by the measurement of viscosity before the actual experiment.

The differential measurements were made at intervals of 2°C. to get  $\Delta\theta$ , the change in the angle of emergence from the prism, using sodium yellow light from a sodium lamp. The thermostatted liquid cell was filled with the experimental solution, and the angle  $\theta'$  was read by taking repeated drum readings when the temperature had become steady to  $\pm 0.02^\circ\text{C}$ . (the temperature was controlled to  $\pm 0.02^\circ\text{C}$ ., and maintained by circulating water from an ordinary controlled bath through the chambers inside and around the

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liquid cell). These measurements were repeated at intervals  $\Delta T=2^{\circ}\text{C}$ . in the range from  $15^{\circ}\text{C}$ . to  $45^{\circ}\text{C}$ . approximately. The change in the reading of the refractometer gives directly the change in the angle of emergence  $\Delta\theta'$ , in minutes of arc, for a given change  $\Delta T$  in temperature. An approximate correction was applied for the effect of the small change in concentration of experimental solution due to evaporation of alcohol in the time elapsing between readings at successive temperatures. This correction was estimated by replacing the original solution by a

fresh one after every ten or twelve degrees centigrade, and the small change (of the order of 20 to 50 seconds) in angle of emergence,  $\theta$ , was evenly divided over the number of sets of observation taken during this period. For the heating sequence, the correction is negative, and for the cooling sequence it is positive.

### Measurements with 2.5%, 5% and 7% Alcohol in Water

A series of observation was first made during

TABLE I (a).—TEMPERATURE, THE READINGS OF DRUM  $\theta$ , AND THE CALCULATED VALUES OF  $\Delta\theta$  (IN MINUTES) FOR  $2^{\circ}\text{C}$ . FOR 2.5% ALCOHOL SOLUTION IN THE RANGE OF  $18^{\circ}\text{C}$ . TO  $47^{\circ}\text{C}$ ., USING SODIUM YELLOW LIGHT.

Heating sequence				Cooling sequence			
Temperature $^{\circ}\text{C}$ .	Drum readings	$\Delta\theta$ for $2^{\circ}\text{C}$ . in minutes	Corrected value of $\Delta\theta$ in minutes	Temperature $^{\circ}\text{C}$ .	Drum readings $^{\circ}\text{C}$ .	$\Delta\theta$ for $2^{\circ}\text{C}$ . in minutes	Corrected value of $\Delta\theta$ in minutes.
				18.0	$3^{\circ}40'52''\pm 1''$	(Fresh solution)	
				18.0	$3^{\circ}40'42''\pm 2''$		
19.0	$3^{\circ}40'4''\pm 1''$	$1'-8''\pm 1''$	$1'-8''-1''=1'.11$			$1'-7''\pm 2''$	$1'-7''+2''=1'.15$
21.0	$3^{\circ}38'56''\pm 0''$	$1'-11''\pm 1''$	$1'-11''-1''=1'.17$	20.0	$3^{\circ}39'35''\pm 1''$	$1'-0''\pm 1''$	$1'-0''+2''=1'.03$
23.0	$3^{\circ}37'45''\pm 1''$	$1'-13''\pm 2''$	$1'-13''-1''=1'.20$	22.0	$3^{\circ}38'35''\pm 1''$	$1'-10''\pm 1''$	$1'-10''+2''=1'.2$
25.0	$3^{\circ}36'32''\pm 2''$			24.0	$3^{\circ}37'25''\pm 1''$	$1'-15''\pm 1''$	$1'-15''+3''=1'.30$
				26.0	$3^{\circ}36'10''\pm 1''$	(Fresh solution)	
		$1'-12''\pm 2''$	$1'-12''-1''=1'.18$	26.0	$3^{\circ}35'55''\pm 1''$	$1'-22''\pm 1''$	$1'-22''+3''=1'.41$
27.0	$3^{\circ}35'20''\pm 4''$	$1'-28''\pm 1''$	$1'-28''-1''=1'.45$	28.0	$3^{\circ}34'33''\pm 0''$	$1'-28''\pm 1''$	$1'-28''+3''=1'.51$
29.0	$3^{\circ}33'52''\pm 0''$	$1'-27''\pm 1''$	$1'-27''-1''=1'.43$	30.0	$3^{\circ}33'5''\pm 1''$	$1'-13''\pm 2''$	$1'-13''+3''=1'.25$
31.0	$3^{\circ}32'25''\pm 1''$	$1'-32''\pm 1''$	$1'-32''-1''=1'.51$	32.0	$3^{\circ}31'52''\pm 2''$	$1'-28''\pm 2''$	$1'-28''+3''=1'.51$
33.0	$3^{\circ}30'53''\pm 1''$						
33.0	$3^{\circ}31'0''\pm 2''$	(Fresh solution)					
		$1'-42''\pm 2''$	$1'-42''-2''=1'.67$	34.0	$3^{\circ}30'24''\pm 1''$	$1'-36''\pm 2''$	$1'-36''+3''=1'.65$
35.0	$3^{\circ}39'18''\pm 1''$	$1'-22''\pm 1''$	$1'-22''-2''=1'.33$	36.0	$3^{\circ}28'48''\pm 2''$	(Fresh solution)	
				36.0	$3^{\circ}28'38''\pm 2''$	$1'-25''\pm 4''$	$1'-25''+2''=1'.45$
37.0	$3^{\circ}27'56''\pm 0''$	$2'-0''\pm 1''$	$2'-0''-2''=1'.97$	38.0	$3^{\circ}27'13''\pm 3''$	$1'-37''\pm 4''$	$1'-37''+2''=1'.65$
39.0	$3^{\circ}25'56''\pm 1''$	$1'-28''\pm 2''$	$1'-28''-2''=1'.43$	40.0	$3^{\circ}25'36''\pm 2''$	$1'-28''\pm 3''$	$1'-28''+3''=1'.51$
41.0	$3^{\circ}24'28''\pm 2''$			42.0	$3^{\circ}24'8''\pm 2''$	$1'-48''\pm 3''$	$1'-48''+3''=1'.85$
41.0	$3^{\circ}24'36''\pm 0''$	(Fresh solution)		44.0	$3^{\circ}22'20''\pm 2''$	(Fresh solution)	
		$1'-44''\pm 1''$	$1'-44''-3''=1'.68$				
43.0	$3^{\circ}22'52''\pm 1''$	$1'-50''\pm 2''$	$1'-50''-3''=1'.78$				
45.0	$3^{\circ}21'2''\pm 2''$	$2'-2''\pm 3''$	$2'-2''-3''=1'.98$				
47.0	$3^{\circ}19'0''\pm 2''$						
47.0	$3^{\circ}19'10''\pm 2''$	(Fresh solution)					

TABLE I (b).—TEMPERATURE, THE READINGS OF DRUM  $\theta$ , AND THE CALCULATED VALUES OF  $\Delta\theta'$  (IN MINUTES) FOR 2°C. FOR 5% ALCOHOL SOLUTION IN THE RANGE OF 13°C. TO 45°C. USING SODIUM YELLOW LIGHT.

Heating sequence				Cooling sequence			
Temperature °C.	Drum readings	$\Delta\theta$ for 2°C. in minutes	Corrected value of $\Delta\theta$ in minutes	Temperature °C.	Drum readings	$\Delta\theta$ for 2°C. in minutes	corrected value of $\Delta\theta$ in minutes
				13.0	3°23'4"±2"	(Fresh solution)	
14.0	3°23'42"±2"	(Fresh solution)		13.0	3°22'56"±2"	1'-0"±2"	1'-0"+1"=1'.01
		1'-0"±3"	1'-0"-1"=0'.98	15.0	3°21'56"±0"	0'-50"±0"	0'-50"+1"=0'.85
16.0	3°22'42"±2"	0-56"±0"	0'-56"-1"=0'.90	17.0	3°21'6"±0"	1'-4"±0"	1'-4"+1"=1'.08
18.0	3°21'46"±1"	1'-19"±1"	1'-19"-1"=1'.30	19.0	3°20'2"±0"	1'-10"±0"	1'-10"+1"=1'.18
20.0	3°20'27"±1"	1'-5"±2"	1'-5"-1"=1'.07	21.0	3°18'52"±0"	1'-15"±1"	1'-15"+1"=1'.25
22.0	3°19'22"±2"	1'-22"±4"	1'-22"-1" 1'.35	23.0	3°17'37"±1"	0'-53"±1"	0'-53"+1"=0'.90
24.0	3°18'0"±3"	1'-12"±4"	1'-12"-1"=1'.18	25.0	3°16'44"±1"	1'-14"±1"	1'-14"+1"=1'.25
26.0	3°16'48"±2"			27.0	3°15'30"±1"	(Fresh solution)	
		1'-19"±2"	1'-19"-1"=1'.30	27.0	3°15'23"±0"		
28.0	3°15'29"±0"					1'-25"±0"	1'-25"+1"=1'.43
28.0	3°15'36"±1"	(Fresh solution)		29.0	3°13'58"±0"	1'-5"±1"	1'-5"+1"=1'.10
		1'-26"±1"	1'26"-2"=1'.40	31.0	3°12'53"±1"	1'-43"±1"	1'-43"+1"=1'.73
30.0	3°14'10"±1"	1'-20"±1"	1'20"-2"=1'.30	33.0	3°11'10"±0"	1'-28"±0"	1'-28"+1"=1'.48
32.0	3°12'50"±0"	1'30"±2"	1'-30"-2"=1'.47	35.0	3°9'42"±0"	1'-42"±2"	1'-42"+1"=1'.72
34.0	3°11'20"±2"	1'-48"±2"	1'-48"-2"=1'.77	37.0	3° 8'0"±2"	(Fresh solution)	
36.0	3°9'32"±1"	1'-52"±2"	1'-52"-2"=1'.83	37.0	3° 8'0"±1"	1'-33"±2"	1'-33"+0"=1'.55
38.0	3°7'40"±2"	1'-24"±5"	1'-24"-2"=1'.37	39.0	3°6'27"±2"	1'-33"±2"	1'-33"+0"=1'.55
40.0	3°6'16"±4"			41.0	3°4'54"±0"	2'-0"±2"	2'-0"+0"=2'.00
				43.0	3°2'54"±2"	1'-44"±5"	1'-44"+0"=1'.73
40.0	3°6'28"±2"	(Fresh solution)		45.0	3°1'10"±4"		

heating sequence with  $\Delta T=2^\circ\text{C}$ ., and then during the cooling sequence, the temperatures of measurement being staggered one degree in the cooling sequence, so as to get an experimental point at each degree from the overall experiment. The r.m.s. deviation for  $\Delta\theta$  is seen from Table I (a), I (b) and I (c) for 2.5, 5 and 7 percent alcohol solution, to be of the order of 3 to 5 seconds of arc. Plots of the results are shown in Fig. 1(a), where the solid circles refer to the rising

temperature sequence, and the crosses are for the falling temperature sequence.

Although there is considerable scatter of the experimental points about the best graphs drawn through these points, the graphs do show a number of maxima and minima. In order to improve the accuracy, the whole series of experiments was repeated and Fig. 1(b) shows the means of the two sets plotted; these graphs show the series of maxima

TABLE I (c).—TEMPERATURE, THE READINGS OF DRUM  $\theta$ , AND THE CALCULATED VALUES OF  $\Delta\theta$  (IN MINUTES) FOR 2°C. FOR 6.8% ALCOHOL SOLUTION IN THE RANGE OF 16°C. TO 41°C., USING SODIUM YELLOW LIGHT.

Heating sequence				Cooling sequence			
Temperature °C.	Drum $\theta$ readings	$\Delta\theta$ for 2°C. in minutes	Corrected values of $\Delta\theta$ in minutes	Temperature °C.	Drum $\theta$ readings	$\Delta\theta$ for 2°C. in minutes	Corrected values of $\theta\Delta$ in minutes
				16.0	3°57'0"±2"	(Fresh solution)	
				16.0	3°56'52"±1"		
				18.0	3°55'52"±1"	1'-0"±1"	1'-0"+1"=1'.01
19.0	3°55'10"±1"	(Fresh solution)		20.0	3°54'52"±1"	1'-0"±1"	1'-0"+1"=1'.01
		1'-22"±1"	1'-22"-2"=1'.33			1'-22"±2"	1'-22"+2"=1'.40
21.0	3°53'48"±0"			22.0	3°53'30"±2"	1'-20"±3"	1'-20"+2"=1'.36
		1'-14"±1"	1'-14"-2"=1'.20	24.0	3°52'10"±2"	1'-20"±2"	1'-20"+2"=1'.36
23.0	3°52'34"±1"			26.0	3°50'50"±0"	(Fresh solution)	
		1'-32"±1"	1'-32"-2"=1'.50	26.0	3°50'20"±2"	1'-26"±2"	1'-26"+6"=1'.53
25.0	3°51'2"±1"			28.0	3°48'54"±1"	1'-29"±1"	1'-29"+6"=1'.58
		1'-28"±1"	1'-28"-2"=1'.43	30.0	3°47'25"±1"	1'-30"±2"	1'-30"+6"=1'.60
27.0	3°49'34"±1"						
		1'-39"±1"	1'-39"-3"=1'.60	32.0	3°45'55"±2"	1'-29"±2"	1'-29"+6"=1'.58
29.0	3°47'55"±1"			34.0	3°44'26"±1"	1'-50"±2"	1'-50"+6"=1'.93
		1'-27"±1"	1'-27"-3"=1'.40	36.0	3°42'36"±2"	(Fresh solution)	
31.0	3°46'28"±1"			36.0	3°42'30"±2"	1'-40"±3"	1'-40"+3"=1'.71
31.0	3°46'43"±1"	(Fresh solution)		38.0	3°40'50"±2"	1'-58"±4"	1'-58"+3"=2'.1
		1'-43"±2"	1'-43"-1"=1'.70	40.0	3°38'52"±3"		
33.0	3°45'0"±2"						
		1'-42"±3"	1'-42"-1"=1'.68				
35.0	3°43'18"±2"						
		1'-42"±2"	1'-42"-1"=1'.68				
37.0	3°41'36"±1"						
		1'-50"±3"	1'-50"-2"=1'.80				
39.0	3°39'46"±3"						
		1'-46"±4"	1'-46"-2"=1'.73				
41.0	3°38'0"±2"						
41.0	3°38'6"±2"	(Fresh solution)					

and minima clearly, the scatter of the points being now much less than the amplitudes of these maxima and minima.

Fig. 2 shows a comparison of these mean graphs with the activation energy curves for 2.5, 5 and 6.9 percent aqueous alcohol solutions, and it is seen

from the vertical broken lines that the minima of  $\frac{\partial\theta}{\partial T}$  correspond very closely with the jumps in the

activation energy, whereas the maxima correspond satisfactorily with the middle of flats of the  $E_{\eta}$  curve.

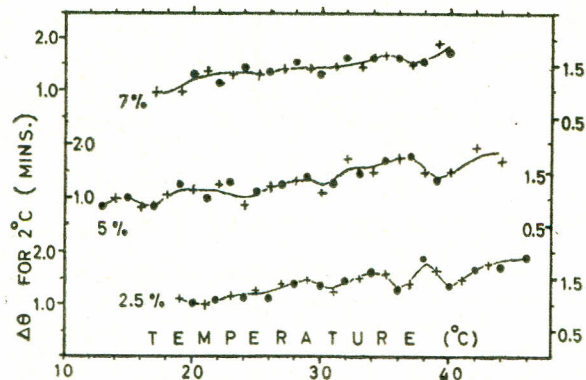


Fig. 1(a).—Plots of the values of  $\Delta\theta$  (in minutes) obtained from differential measurements with intervals of  $2^\circ\text{C}$ . for 2.5%, 5% and 7% aqueous alcohol solutions. ( $\Delta\theta = 1.1 \times \Delta n / \Delta T \times 10^4$ ) The solid circles are for the measurements during the heating sequence and the crosses for the cooling sequence.

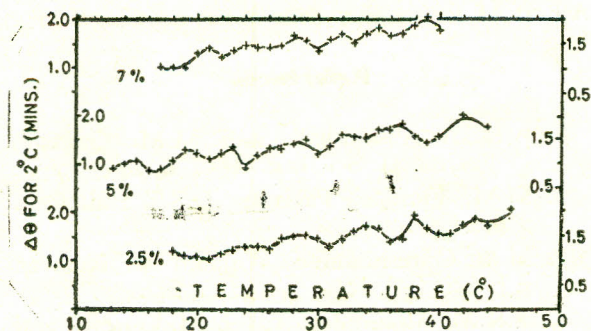


Fig. 1(b).—Plots of the means of the above and a repeated set of similar observations for  $\Delta\theta$  (in minutes), again with intervals of  $2^\circ\text{C}$ . The diminished scatter of the points results in more regular graphs, which bring out the periodic variation in  $\Delta\theta = 1.1 \times \Delta n / \Delta T \times 10^4$  very clearly.

#### 4. Measurements on 8% and 11% Alcohol and Discussion

Similar measurements were made on 7.9% and 10.8% aqueous alcohol, and Fig. 3 presents a comparison of the mean graphs of  $\frac{\partial\theta'}{\partial T}$  for these solutions with graphs of activation energy for nearly corresponding concentrations. Here again, the  $\frac{\partial\theta'}{\partial T}$  curves are roughly sinusoidal, and the minima correspond very closely with the jumps

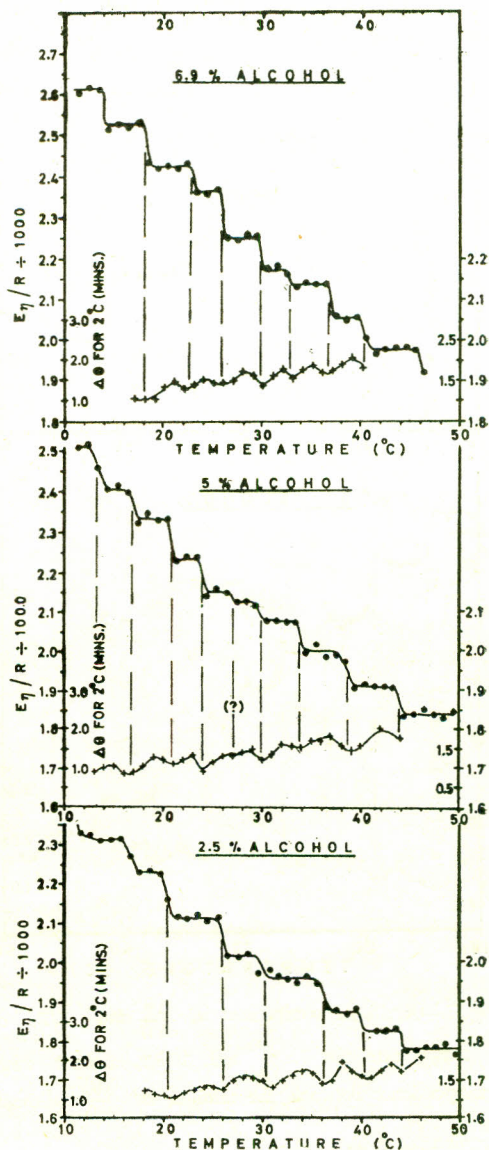


Fig. 2.—Graphical comparison of the curves for  $\frac{\Delta\theta}{\Delta T}$  and  $E\eta/R$  against temperature for 2.5%, 5% and 7% aqueous alcohol. The minima of  $\frac{\Delta\theta}{\Delta T}$  are seen to be very nearly coincident with the jumps in  $E\eta$  curves of corresponding concentration.

in the corresponding  $E\eta$  curve. However, it should be noted that the scatter of the points in the graphs is somewhat greater at the higher concentrations, possibly due to the inadequacy of the correction for changing concentration due to loss of alcohol. Also, it should be noted that

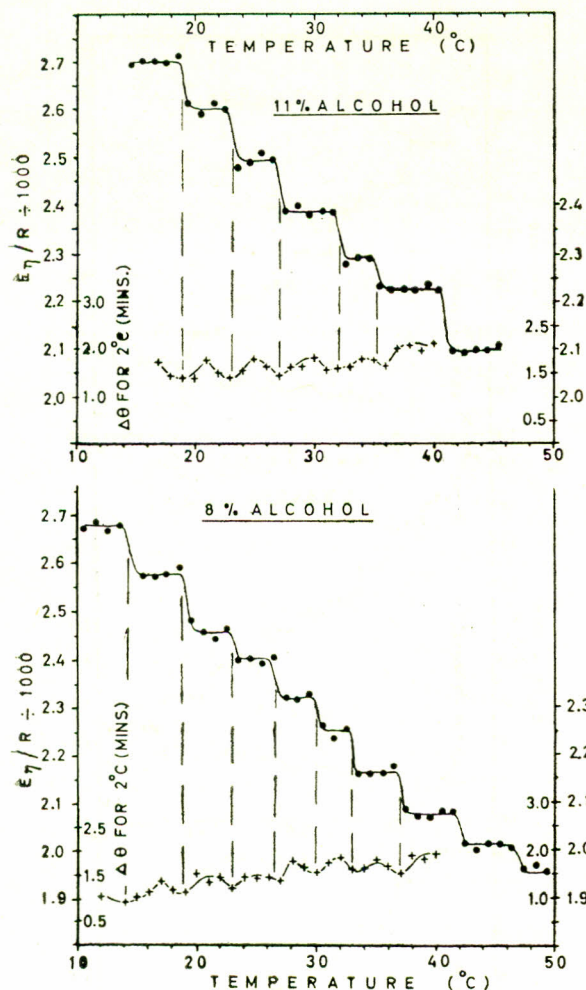


Fig. 3.—A similar comparison of  $\frac{\Delta\theta}{\Delta T}$  and  $E/R$  curves against temperature for 7.9% and 10.8% alcohol solutions. The correspondence between the minima in  $\frac{\Delta\theta}{\Delta T}$  and the jumps in  $\frac{E}{R}$  is again evident.

in the preliminary report on  $\frac{\partial n}{\partial T}$  for pure water, only four consecutive minima from 14°C. to 34°C. were found to fit in with the jumps in  $E/R$ , while this correspondence broke down above 34°C.

Thus, it can be concluded that, in dilute aqueous alcohol, the minima of  $\frac{\partial\theta'}{\partial T}$  are nearly coincident with the jumps in  $E_\eta$ . While this conclusion is very valuable from the fundamental standpoint, it has a further special feature in that it holds promise of utilisation as a relatively easy and less time-consuming technique of interpolating data between the various curves for  $E/R$  already reported by the authors. In this way, it is probable that much more light can be shed on the changes in the jumps in  $E_\eta/R$  as the concentration of the alcohol solution is varied.

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