THE INFLUENCE OF TEMPERATURE ON THE POLARITY OF STATIONARY PHASES USED IN GAS-LIQUID CHROMATOGRAPHY

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(Received February 17th, 1971)

SUMMARY

The present work is an attempt to assess the influence of the temperature on the polarity of the liquid phase in gas chromatography.

This effect was investigated for twenty-one liquid phases of various types of structure. It was found that the polarity depends on the temperature linearly, and its temperature coefficient can be negative, positive or zero.

It is thought, that the data obtained as a result of this work could be of practical use in gas-liquid chromatography.

INTRODUCTION

One of the most important properties of the stationary phases used in gas-liquid chromatography (GLC) is undoubtedly their polarity. As is evident from reference data however, the dipole moment of the liquid phase can not be used as a simple measure for it[1].

Some years ago ROHRSCHNEIDER[2] suggested an empirical method for the determination of the relative polarity of the liquid phase. This method, in spite of some weak points, has proved to be very satisfactory in the field of GLC.

According to this method, the polarity P could be calculated from the expression

$$P = 100 \frac{q_x - q_2}{q_1 - q_2} \tag{1}$$

where q_1, q_2 and q_x are the ratios of the specific retention volumes of butadiene-butane measured on columns coated with β,β'-oxydipropionitrile, squalane and the liquid phase under investigation, respectively.

The use of butadiene-butane as a standard pair, however, is associated with some difficulties and later authors[3], who intended to make the method more general, suggested a better pair: benzene-cyclohexane. These compounds can be found readily in every laboratory and it is possible to measure the polarity at higher temperatures with them, than with the butadiene-butane pair.

It can be assumed that the polarity calculated from eqn. 1 does not, in practice, depend on the temperature of the determination of the retention volumes, if it is one and the same for both the standard phases and for the phase under investigation.

In our earlier measurements it was observed that in some cases the polarity of the stationary phase, found according to ROHRSCHNEIDER depends on the temperature of the experiment. This effect is sometimes higher than the experimental error and must not be neglected.

The present study is an attempt to ascertain the effect of the column temperature on the gas chromatographic polarity of some stationary phases and to demonstrate the cases, in which it is necessary to take this influence into account.

EXPERIMENTAL

The necessary specific retention volumes of benzene and cyclohexane on the β,β'-oxydipropionitrile, squalane and the other stationary phases were measured with a "Fractovap" model B apparatus produced by Carlo Erba, Italy.

Pure dry nitrogen was used as carrier gas. The outlet flow rate in all experiments was 40 ml/min. The outlet pressure was atmospheric pressure, corrected for the water vapour in the soap flowmeter at its temperature. The stainless steel chromatographic column was 2 m long and had an I.D. of 4 mm. Column packing was "Sterchamol" (particle size diam. 0.2–0.3 mm) and the stationary phase consisted of 20% (w/w) of the inert support.

The measurements were carried out at intervals of 10°. The first and the last

TABLE I

SPECIFIC RETENTION VOLUMES OF BENZENE (ml)

No.	Stationary phase	Temperature (°C)							
		50	60	70	80	90	100	110	120
1	Squalane	177.7	133.2	102.9	77.1	61.6	47.6	38.0	31.4
2	β,β'-Oxydipropionitrile	142.9	105.3	80.3	59.2	46.7	35.6	28.1	22.9
3	Diphenyl ether	—	229.2	167.8	118.1	89.9	—	—	—
4	m-Bis-(m-phenoxyphenoxy)benzene	—	—	91.6	67.2	52.7	40.0	31.4	—
5	Glycerol	—	8.6	7.0	5.6	4.7	3.8	—	—
6	Diacetin	113.3	91.2	75.2	51.1	42.1	—	—	—
7	Triacetin	202.9	157.6	125.9	80.3	64.2	—	—	—
8	Diglycerol	11.4	9.1	7.5	6.0	5.0	—	—	—
9	Diethanolamine	28.0	24.8	22.2	17.8	—	—	—	—
10	Triethanolamine	—	39.2	29.8	21.8	17.1	13.0	—	—
11	β,β'-Iminodipropionitrile	—	99.2	74.7	54.4	42.5	32.0	—	—
12	1,2,3-Tris-(2-cyanoethoxy)-propane	—	81.6	63.0	47.1	37.6	29.1	—	—
13	1,2,3,4,5,6-Hexakis-(2-cyanoethoxy)-hexane		46.2	35.0	25.7	20.1	15.3	—	—
14	Adipic dinitrile	226.6	157.2	113.7	78.9	59.4	—	—	—
15	Butanediol-1,4	56.6	44.8	36.4	24.0	19.5	—	—	—
16	Octanediol-1,8	—	—	57.9	43.7	35.2	27.4	22.0	—
17	Decanediol-1,10	—	—	—	49.9	39.2	29.7	23.3	18.9
18	Dodecanediol-1,12	—	—	—	52.4	41.2	31.2	24.5	19.9
19	Thiodiglycol	—	38.8	30.0	22.4	17.9	—	—	—
20	Diethylene glycol	—	50.1	38.3	28.3	22.4	—	—	—
21	Triethylene glycol	—	58.6	47.5	37.5	31.2	—	—	—
22	Tetraethylene glycol	—	65.2	51.8	40.0	32.7	—	—	—
23	Polyethylene glycol 400	—	94.2	70.9	51.5	40.1	30.2	—	—

temperatures of the interval were chosen depending on the melting point and the vapour pressure of the corresponding liquid phases.

The stationary phases under investigation are shown in Table I. All of them were of commercial origin.

At present some of these stationary phases are used widely in gas chromatography, the rest were included in the work in order to show the influence of some structural changes in the molecule of the phases on the function $P = f(t^0)$.

The first measurements showed that the value of the polarity is very sensitive to the errors in the values of the retention volumes, especially when they have equal signs.

For this reason, the values of all retention volumes in the present work are the arithmetic mean of 10 consecutive measurements.

RESULTS AND DISCUSSION

The specific retention volumes of benzene and cyclohexane on the standard and investigated stationary phases at different temperatures are shown in Tables II and III.

In eqn. 1, the denominator does not depend on the stationary phase and changes only with the change of temperature. Fig. 1 shows that the difference $q_1 - q_2$ de-

TABLE II

SPECIFIC RETENTION VOLUMES OF CYCLOHEXANE (ml)

| No.	Stationary phase	Temperature (°C)							
		50	60	70	80	90	100	110	120
1	Squalane	235.9	172.7	130.8	95.8	75.1	56.9	44.7	36.3
2	β,β'-Oxydipropionitrile	15.1	12.7	10.9	9.1	8.0	6.8	6.0	5.3
3	Diphenyl ether	—	125.3	92.3	65.4	50.0	—	—	—
4	m-Bis-(m-phenoxyphenoxy) benzene	—	—	45.9	34.5	27.7	21.5	17.2	—
5	Glycerol	—	5.7	4.3	3.1	2.4	1.8	—	—
6	Diacetin	24.6	20.8	17.9	13.3	11.4	—	—	—
7	Triacetin	46.1	38.4	32.7	23.7	20.2	—	—	—
8	Diglycerol	4.4	3.5	2.8	2.2	1.8	—	—	—
9	Diethanolamine	4.1	3.7	3.5	2.9	—	—	—	—
10	Triethanolamine	—	7.2	6.2	5.3	4.6	4.0	—	—
11	β,β'-Iminodipropionitrile	—	12.6	10.6	8.7	7.5	6.3	—	—
12	1,2,3-Tris-(2-cyanoethoxy)-propane	—	10.0	8.5	7.1	6.1	5.2	—	—
13	1,2,3,4,5,6-Hexakis-(2-cyanoethoxy)-hexane	—	6.7	5.7	4.8	4.2	3.6	—	—
14	Adipic dinitrile	29.6	23.3	18.8	14.8	12.3	—	—	—
15	Butanediol-1,4	19.0	15.3	12.6	8.5	7.2	—	—	—
16	Octanediol-1,8	—	—	28.8	22.5	18.6	15.0	12.4	—
17	Decanediol-1,10	—	—	—	29.6	23.2	17.5	13.7	11.1
18	Dodecanediol-1,12	—	—	—	32.2	25.6	19.7	15.7	12.9
19	Thiodiglycol	—	6.8	6.0	5.3	4.8	—	—	—
20	Diethyleneglycol	—	10.1	8.0	6.2	5.0	—	—	—
21	Triethylene glycol	—	11.0	10.0	9.0	8.3	—	—	—
22	Tetraethylene glycol	—	12.7	11.3	9.9	8.9	—	—	—
23	Polyethylene glycol	—	16.3	14.3	12.5	11.2	9.8	—	—
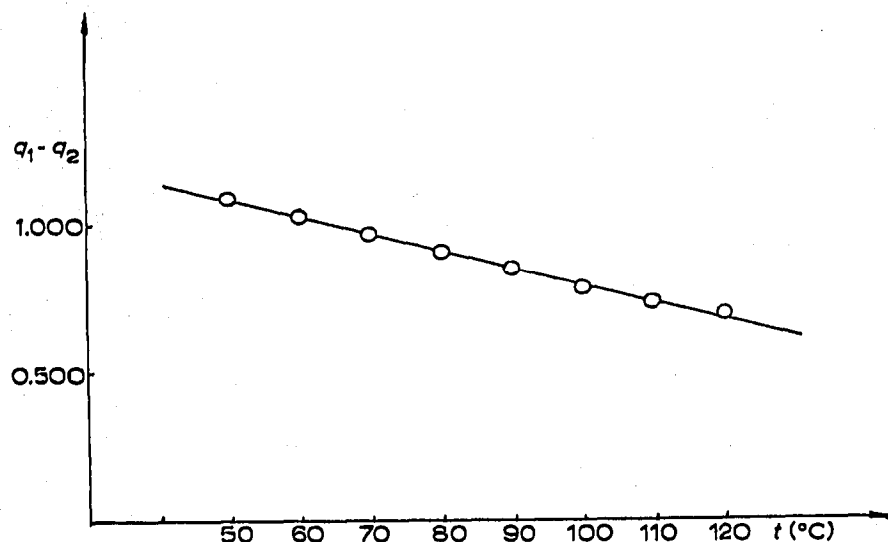
Fig. 1. Plot of the difference q_1-q_2 (eqn. 1) vs. temperature.

creases linearly when the temperature increases. It is evident, that the polarity P according to eqn. 1 will be independent of temperature only if the numerator changes in the same way. The data for the polarities at different temperatures (Table III) show that this condition is only fulfilled in a few cases.

TABLE III

POLARITIES OF THE LIQUID PHASES AT DIFFERENT TEMPERATURES

| No.	Stationary phase	Temperatures (°C)							
		50	60	70	80	90	100	110	120
1	Squalane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	β,β'-Oxydipropionitrile	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
3	Diphenyl ether	—	36.5	37.4	39.0	40.0	—	—	—
4	m-Bis-(m-phenoxyphe-noxy)-benzene	—	—	41.4	42.3	43.0	43.6	44.8	—
5	Glycerol	—	28.6	33.0	39.0	44.1	50.7	—	—
6	Diacetin	71.7	73.3	74.8	75.1	76.4	—	—	—
7	Triacetin	69.9	70.4	70.9	69.0	69.0	—	—	—
8	Diglycerol	48.8	51.9	54.8	59.2	62.7	—	—	—
9	Diethanolamine	87.3	90.6	93.8	96.9	—	—	—	—
10	Triethanolamine	—	82.2	80.7	78.8	77.0	74.7	—	—
11	β,β'-Iminodipropionitrile	—	98.0	98.0	98.2	98.3	98.5	—	—
12	1,2,3-Tris-(2-cyano-ethoxy)-propane	—	99.3	100.2	101.5	102.7	104.2	—	—
13	1,2,3,4,5,6-Hexakis-(2-cyanoethoxy)-hexane	—	92.2	91.5	90.7	89.9	88.9	—	—
14	Adipic dinitrile	91.8	91.5	91.1	90.7	90.3	—	—	—
15	Butanediol-1,4	54.5	56.4	58.2	60.4	61.2	—	—	—
16	Octanediol-1,8	—	—	41.8	42.3	42.5	42.7	43.2	—
17	Decanediol-1,10	—	—	—	35.8	36.8	38.3	40.5	42.2
18	Dodecanediol-1,12	—	—	—	35.8	34.3	34.6	35.5	36.1
19	Thiodiglycol	—	84.6	82.3	79.6	77.1	—	—	—
20	Diethylene glycol	—	78.3	80.6	83.6	86.2	—	—	—
21	Triethylene glycol	—	81.3	80.2	78.8	77.4	—	—	—
22	Tetraethylene glycol	—	79.8	78.7	77.6	76.5	—	—	—
23	Polyethylene glycol	—	84.9	82.0	78.5	75.3	71.0	—	—
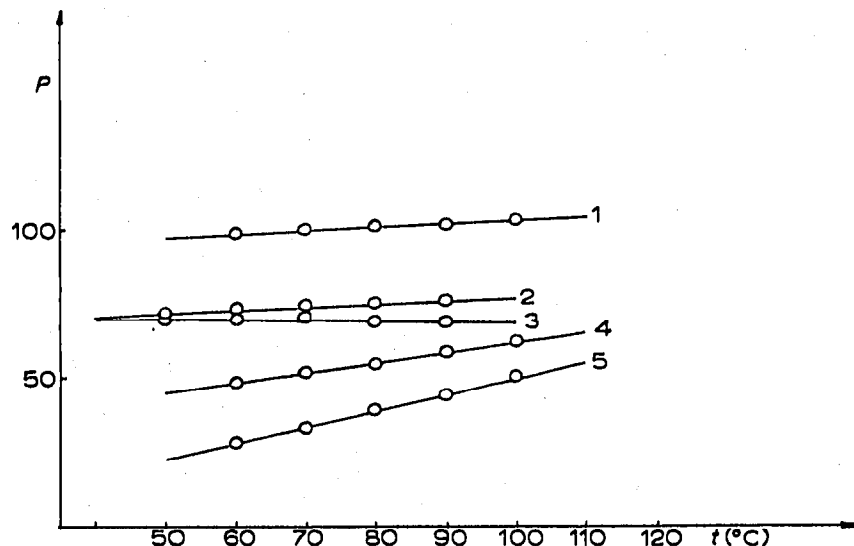
Fig. 2. Dependence of the polarity of the liquid phase on the temperature. 1 = 1,2,3-tris-(2-cyanoethoxy)-propane; 2-diacetin; 3 = triacetin; 4 = diglycerol; 5 = glycerol.

From a formal view-point, the phases under investigation could be divided into three groups.

In the first group are the phases where the increase of the temperature leads to an increase in the polarity, *e.g.* $\Delta P / \Delta t > 0$. These are phases such as diethylene glycol; butanediol-1,4; decanediol-1,10; 1,2,3-tris-(2-cyanoethoxy)-propane; diethanolamine; glycerol; diglycerol; diacetin; diphenyl ether and *m*-bis-(*m*-phenoxy-phenoxy)-benzene.

The second group includes the liquid phases 1,2,3,4,5,6-hexakis-(2-cyanoethoxy)-hexane; triethylene glycol; tetraethylene glycol; polyethylene glycol 400; thiodi-
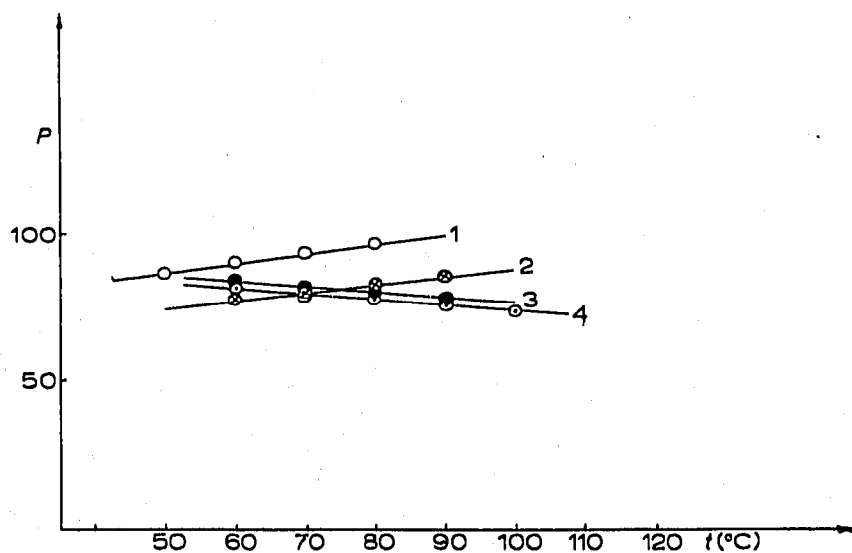
Fig. 3. Polarity of the liquid phases depending on the temperature. 1 = diethanolamine; 2 = diethylene glycol; 3 = thiodiglycol; 4 = triethanolamine.

glycol and triethanolamine. They decrease the polarity when the temperature increases *e.g.* $\Delta P/\Delta t < 0$.

The third group includes those phases whose polarity is practically temperature independent, $\Delta P/\Delta t = 0$, for example β,β'-iminodipropionitrile; triacetin; adipic-dinitrile; octanediol-1,8 and dodecanediol-1,12.

Fig. 2 presents graphically the relationship $P = f(t^0)$ for glycerol and other phases, which are glycerol derivatives. Acetylation or cyanoethylation of the glycerol hydroxy groups leads to a decrease in the slope of the lines. For instance $\Delta P/\Delta t$ is about +0.55 units/degree for the glycerol, while the same quantity is +0.10 and +0.13 units/degree for diacetin and 1,2,3-tris-(2-cyanoethoxy)-propane. In the case of triacetin the slope of the line becomes negative (−0.05 units/degree).

In addition, diglycerol has a lower temperature coefficient than glycerol. In this case the total number of the hydroxy groups, as compared with glycerol, is higher but their percentage per unit molecular weight is lower. On the other hand in the diglycerol molecule there is a new structural element—the ether bond.

The dependence between polarity and temperature for diethanolamine, diethylene glycol, thiodiglycol and triethanolamine is shown in Fig. 3. The common
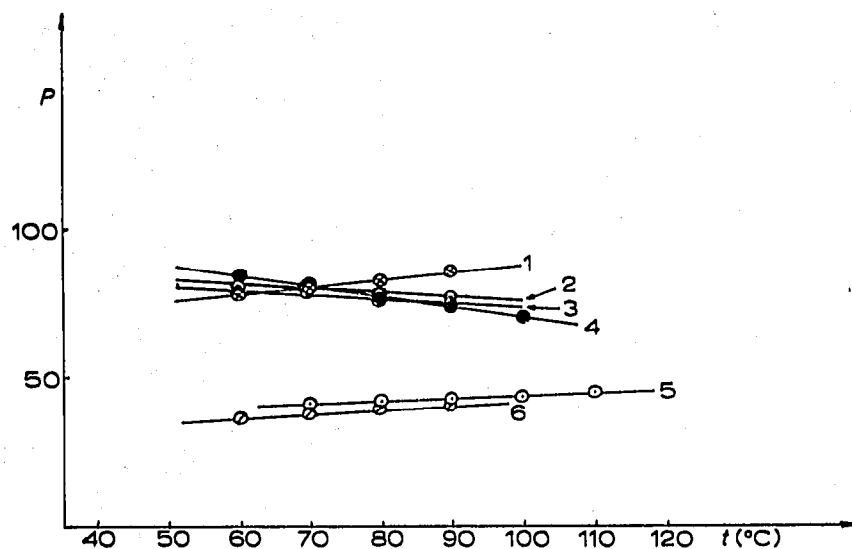

Fig. 4. Plot of the polarity of the liquid phases *vs.* temperature. 1 = diethyleneglycol; 2 = triethylene glycol; 3 = tetraethylene glycol; 4 = polyethylene glycol 400; 5 = *m*-bis-(*m*-phenoxy-phenoxy)-benzene; 6 = diphenyl ether.

feature in the structure of these liquid compounds is the presence of 2-hydroxyethyl groups. The first three of them differ only in the heteroatom in the chain.

Examination of the functions $P = f(t^0)$ in Fig. 3 shows that diethylene glycol and diethanolamine have almost equal positive slopes while thiodiglycol and triethanolamine have almost equal but negative slopes. A very interesting fact is the great difference in the temperature coefficient of polarity in the case of thiodiglycol as compared with diethylene glycol and diethanolamine.

Fig. 4 shows the graphical presentation of the changes in the polarity of some ethylene glycols with change of temperature. It can be seen that the highest temper-
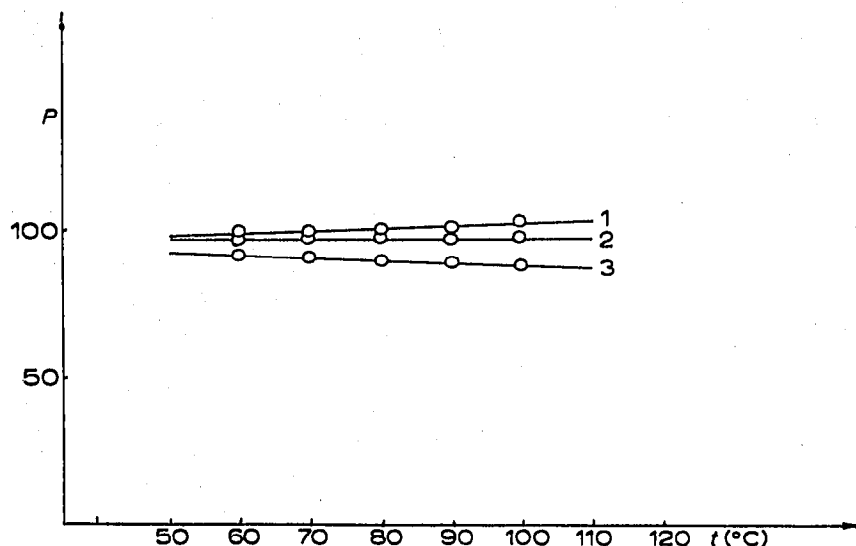
Fig. 5. Polarity of the liquid phases as a function of temperature. 1 = 1,2,3-tris-(2-cyanoethoxy)-propane; 2 = β,β'-iminodipropionitrile; 3 = 1,2,3,4,5,6-hexakis-(2-cyanoethoxy)-hexane.

ature coefficient of polarity (positive value) is shown by diethylene glycol. The increase in the number of –OCH_2CH_2– groups leads to a decrease in the slopes (already negative) of triethylene and tetraethylene glycols and polyethylene glycol 400. The polyethylene glycol-400 line has the most negative slope. Data concerning diphenyl ether and m-bis-(m-phenoxyphenoxy)-benzene are shown in the same figure. The line for diphenyl ether has a higher positive temperature coefficient of polarity than the second liquid phase, but the difference is not very great.

The data concerning liquid phases with propionitrile groups are given in Fig. 5. It can be seen that β,β'-iminodipropionitrile has a practically constant polarity and it has a value close to the value of the standard β,β'-oxydipropionitrile (P = 100).
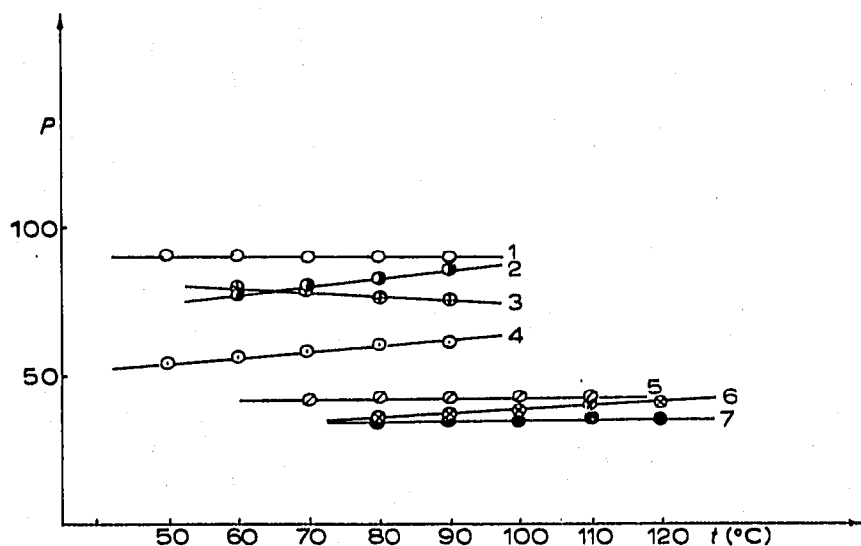

Fig. 6. Dependence of the polarity of the liquid phases on the temperature. 1 = Adipic dinitrile; 2 = diethylene glycol; 3 = tetraethylene glycol; 4 = butanediol-1,4; 5 = octanediol-1,8; 6 = decanediol-1,10; 7 = dodecanediol-1,12.

This means that the substitution of an imino group by an ether bond does not influence the temperature coefficient $\Delta P/\Delta t$.

An increase in the number of the propionitrile groups in the molecule of the phase decreases the slope of the line $P = f(t^0)$ from a positive to a negative value (e.g. see 1,2,3-tris-(2-cyanoethoxy)-propane and 1,2,3,4,5,6-hexakis-(2-cyanoethoxy)-hexane).

Study of the influence of the temperature on the polarities of phases from the group of alkanediols (Fig. 6) shows that butanediol-1,4 and decanediol-1,10 have almost equal positive temperature coefficients, $+0.17$ and $+0.16$ units/degree, respectively.

Octanediol-1,8 and dodecanediol-1,12 are similar in their behavior too, but differ from the first two diols. It is now difficult to explain why there is no regular change of the slope of $P = f(t^0)$ for all diols.

The presence of an extra ether bond in diethylene glycol as compared with butanediol-1,4 hardly changes the slope of the line (Fig. 6); however the accumulation of several ether bonds (e.g. tetraethylene glycol as compared with octanediol-1,8) leads to a considerable difference. In this case tetraethylene glycol has the same number $-OH$ and $-CH_2-$ groups as octanediol-1,8, but has three $-O-$ bonds more.

The exchange of both hydroxy groups in butanediol-1,4 with nitrile groups in adipic dinitrile makes the polarity of the liquid phase almost independent of temperature.

In conclusion it might be summarized that:

(1) Polarity of the liquid phase depends linearily on the temperature.

(2) The dependence between the polarity and temperature can have a positive, negative or zero temperature coefficient.

(3) In a given temperature interval one liquid phase can be more polar than another phase, but they can exchange their polarities in another temperature interval.

REFERENCES

1 H. ROTZSCHE AND M. HOFMANN, in E. LEIBNITZ AND H. G. STRUPPE (Editors), *Handbuch der Gas-Chromatography*, Verlag Chemie, Weinheim/Bergstr., 1967, p. 351.
2 L. ROHRSCHNEIDER, *Z. Anal. Chem.*, 170 (1959) 256.
3 P. CHOVIN AND J. LEBBE, *Communication aux Journées International d'Étude des Méthodes de Séparation Immédiate et de Chromatographie, juin 1961, Paris.*