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# SEPARATION OF ISOTOPICALLY SUBSTITUTED POLAR COMPOUNDS DERIVED FROM HYDROCARBONS

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#### SUMMARY

The separation of isotopically substituted  $C_1-C_3$  alcohols, acetone and pyridine was studied and some thermodynamic parameters were determined. It was found that the retention order for pyridine and deuteropyridine can be correlated with their molecular weights.

## INTRODUCTION

The separation of isotopically substituted polar compounds is a difficult problem, and has been described by CARTONI *et al.*<sup>1</sup>.

The present paper deals with the separation of a number of polar compounds on comer capillary columns with polar stationary phases, and also with the determination of some thermodynamic functions of the dissolution of these compounds.

All the experiments were carried out on a Becker Delft chromatograph with a flame ionization detector. Nitrogen was used as the carrier gas. The separation was carried out on capillary columns coated with various stationary phases. Their length was 50-60 m, and their efficiency was about 100,000 theoretical plates for *n*-heptane.

Before coating the liquid stationary phase, all the columns were treated with oxygen at  $250^{\circ}$  and 4-5 atm for 5-6 h. To improve the shape of the peaks, a surfaceactive substance was added (5% of the weight of the stationary phase) to the stationary phase solution. All the retention volumes of the components were measured, taking methane as the non-sorbed component.

# SEPARATION OF ALCOHOLS

The resolution of the isotopic methanol-deuteromethanol, ethanol-deuteroethanol and isopropanol-deuteroisopropanol mixtures was carried out on capillary columns with polyethylene glycol (PEG)-400, -600 and -1000 and with polypropylene glycol 1025 (PPG-1025).

Samples of  $1 \mu l$  were introduced into the column with a splitter (splitting ratios 1:50 and 1:100). The separation time was about 30 min at a flow-rate of the carrier gas of 1 ml/min (Fig. 1). In all the cases considered, the retention times of the deutero compounds were found to be shorter, *i.e.*, an inverse isotopic effect

took place. The variation of the logarithm of the ratios of retention volumes as a function of the reciprocal of the temperature is shown in Fig. 2.

By using chromatographic values, the differences in the enthalpies and entropies for these systems were calculated (Table I). From the values of the ratio of vapour



Fig. 1. Separation of  $C_1-C_3$  alcohols on PEG-1000. (a)  $CH_3OH-CD_3OH$ , 42°, 1.1 ml/min; (b)  $C_2H_5OH-C_2D_5OH$ , 46°, 1.15 ml/min; (c) iso- $C_3H_7OH$ -iso- $C_3D_7OH$ , 44°, 1.1 ml/min.



Fig. 2. Coefficient of separation for alcohols on different stationary phases. iso- $C_3H_7OH$ -iso- $C_3D_7OH$  on (1) PEG-1000, (2) PEG-600, (3) PEG-400;  $C_2H_5C_{--}C_2D_5OH$  on (4) PEG-1000, (5) PEG-600, (6) PEG-400;  $CH_3OH$ - $CD_3OH$  on (7) PEG-600, (8) PEG-1000, (9) PEG-400.

pressures and retention volumes<sup>1</sup>, the ratio of the activity coefficients,  $\gamma_D/\gamma_H$ , at different temperatures was calculated for the CH<sub>3</sub>OH-CD<sub>3</sub>OH system (Table II).

From Table II, it can be seen that the value of the log  $(V_{R(H)}/V_{R(D)})$  ratio of the pair CH<sub>3</sub>OH-CD<sub>3</sub>OH is larger than the ratio of their vapour pressures and, accordingly, the resolution of isotopically substituted alcohol mixtures on polar stationary phases is better than would be expected from the differences in their vapour pressures. The activity coefficient ratio,  $\gamma_D/\gamma_H$ , of the CH<sub>3</sub>OH-CD<sub>3</sub>OH pair is not equal to unity, it decreases with increase in temperature and depends on the polarity of the phases. Analogous relationships are observed for other mixtures. On PEG and PPG columns, the isopropanol-deuteroisopropanol mixture was resolved better than were other mixtures.

As the polarity of the stationary phases decreased, the resolution for all the pairs increased. The best resolutions were achieved on PEG-1000 and PPG-1025.

For the  $CH_3OH-CD_3OH$  pair at temperatures above 50°, the resolution on PEG-1000 was found to be better than on PEG-600, while at temperatures below 50° the reverse was true.

## SEPARATION OF ACETONES

The separation of the  $CH_3COCH_3-CD_3COCD_3$  mixture was achieved on PEG-400, -600, -1000 and PPG-1025 columns in the 35-60° temperature range. The carrier gas flow-rate was 1.1 ml/min. The differences in the enthalpies and entropies in the chromatographic separation are given in Table I. The plots of log  $(V_{R(H)}/V_{R(D)})$  against 1/T are shown in Fig. 3. In all the cases investigated, deuteroacetone was the st to be eluted. The resolution was found to be best on PEG-1000 and PPG-



Fig. 3. Separation of acetones and temperature dependence of coefficient of separation, on (1) PEG-400, (2) PEG-600 and (3) PEG-1000.

TABLE I

INFFERENCES IN THE ENTHALPIES (ca<sup>1</sup>/mole) AND ENTROPIES (ca<sup>1</sup>/mol<sup>-</sup> C, × 10<sup>2</sup>) FOR SOME SYSTEMS ON POLAR STATIONARY PHASES ŝ 4 ÷

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$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		HII HII	1S <sub>11</sub> - 1S <sub>10</sub>	MIR . MIR	IS <sub>H</sub> IS <sub>h</sub>	$H_{H} = H_{B}$	1Sn 1Sp	$AH_{H} - AH_{D}$	$dS_{H} = dS_{H}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	110"(1.) 140"[1,	- 16.4	0.51		0.71	- 40.0	- 6.84	- 24.60	- 1.00
$ \begin{array}{ccccc} AF(0) & 40.6 & 7.71 & 33.9 & -2.70 & 34.4 & -2.07 & -40.20 \\ CH_2(0CH)_3 & CD_3(0CD)_3 & 15.8 & \pm 1.40 & 0.53 & 14.4 & -2.07 & -40.20 \\ CH_3(0CD)_3 & 15.8 & \pm 1.40 & 0.53 & 14.4 & -2.07 & -40.20 \\ TABLE H & TADE & $	HON CAROL	0.42	74-1	15.0	1.05	32.0	- 2.95	15.00	- 19.60
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	so-C <sub>3</sub> H <sub>2</sub> OH iso-C <sub>3</sub> D <sub>2</sub> OH	9.6t	1.7.1	33.0		34-4	70.5	40.20	- 6.00
TARLE II RATIOS OF RETEXTIONS $\Gamma'_{R(II)} T'_{R(II)}$ . VAPOUR PRESSURES, $P_{IP} P_{II}$ , AND COEFFICTENTS OF ACTIVITY, $P_{II} P'_{PI}$ , FOR THE CH <sub>3</sub> OH CI RATIOS OF RELEXTIONS $\Gamma'_{R(II)} T'_{R(II)}$ . Main any phase $(C) D_{II}$ $D_{II}$ $Main any phase (C) D_{II} D_{II} Main any phase (C) D_{II} D_{II} Main any phase 1''_{R(II)} D_{II} D_{II} D_{II} Main any phase 1''_{R(II)} D_{II} $	JH <sub>s</sub> COCH <sub>a</sub> CD <sub>s</sub> COCD <sub>a</sub> JH <sub>s</sub> S C <sub>5</sub> D <sub>s</sub> N	15.8	÷ 1.49 + 1.1.6	65.3 00.82	+++ +++	- 40-7 - 50-30	- 5.03 		+ 3.70
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40     1.00720     1.0240     1.0240     1.031       41     1.00724     1.0240     1.030     1.025       42     1.00724     1.0166     1.030     1.025       43     1.00724     1.0260     1.026     1.0213       46     1.00752     1.0155     1.0273     1.0211       49     1.00752     1.0155     1.026     1.0211       40     1.00750     1.0232     1.0155     1.0333       50     1.00750     1.0228     1.0216     1.0203       51     1.00760     1.0228     1.0168     1.0202       52     1.00780     1.0148     1.0236     1.0103       53     1.0070     1.0228     1.0168     1.0202       54     1.0078     1.0188     1.0265     1.0333       55     1.0071     1.0220     1.0168     1.0202       56     1.00800     1.0220     1.0168     1.0162       55     1.00812     1.0213     1.0213     1.0323       56     1.00812     1.0213     1.02168     1.0162       57     1.00812     1.0168     1.0168     1.0162		1. <sup>, R(D)</sup>	у.н	( <i>u</i> ) <i>u</i> , 1	1.1	1.' <i>n(</i> 1))	<i>n.</i> :	1"'R(M	л.
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12     1.00728     1.0372     1.0300     1.025     1.0344       10     1.00744     1.037     1.037     1.034     1.0213     1.0344       10     1.00750     1.0232     1.015     1.0284     1.0211     1.0345       10     1.00750     1.0232     1.0155     1.0284     1.0211     1.0335       55     1.00760     1.0228     1.0148     1.0205     1.0333       60     1.00800     1.0228     1.0188     1.0202     1.0333       61     1.00810     1.0228     1.0188     1.0218     1.0333       63     1.00810     1.0228     1.0188     1.0280     1.0333       63     1.00812     1.0220     1.0188     1.0283     1.0333	trijoon 1	07201	9910.1			•	# 4 · · · ·	1.0340	1.0275
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48     1.00752       1.0211        40     1.00750     1.0232     1.0155          50     1.00700       1.0204     1.0202     1.033       55     1.00700       1.0205     1.0188     1.0202     1.033       60     1.00700       1.0236     1.0188     1.0262     1.033       63     1.00800       1.0230     1.0188     1.0283     1.0346       63     1.00812     1.0220     1.0188     1.0283     1.0346     1.0346       63     1.00812     1.0220     1.0108     1.0265     1.0183     1.0326	1t200'1 01	* * *	and the second	1.0.30	1.0223		*	1.0344	1.0268
40     1.00750     1.01232     1.0155         50     1.00700      1.0204     1.0206     1.0202     1.033       55     1.00700      1.0148     1.0208     1.0102     1.032       60     1.00800      1.0226     1.0148     1.0283     1.0188     1.0272     1.0183       63     1.00810       1.0250     1.0188     1.0183     1.0324       63     1.00812     1.0220     1.0138     1.0188     1.0183     1.0324	1,00752				5	1.0288	1.0211	Norman	** - san 1
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1025. At temperatures below  $37^{\circ}$ , the resolution on PEG-600 was better than that on PEG-400, and above  $37^{\circ}$  the reverse was true.

#### SEPARATION OF PYRIDINES

The separation of the  $C_5H_5N-C_5D_5N$  mixture was carried out on PEG-400, -600 and -1000 columns in the range 40–65°. The time of separation was about 1 h. The results obtained are presented in Fig. 4. In all cases, deuteropyridine emerged from the column later than pyridine, owing to the stronger interaction of deuteropyridine with PEG. Hence, in this particular case, a normal isotopic effect was observed for this mixture.



Fig. 4. Separation of pyridines and temperature dependence of coefficient of separation, on (1) PEG-460, (2) PEG-600 and (3) PEG-1000.

# DISCUSSION

It is known that the average length of the C-D bond is shorter than that of the C-H bond by 0.004-0.005 Å. This leads to a difference in the polarizabilities of the deuterated and hydrated molecules and to a difference in their polarities and dipole moments. The lower the number of C-D bonds in a molecule, the greater are these differences. The separation of deutero-substituted non-polar molecules on non-polar liquid phases is determined mainly by the difference in their vapour pressures, and the separation of mixtures of polar molecules is determined mainly by the difference

Mixture	$\frac{V'_{R(H)}}{V'_{R(D)}}$		$\frac{\Delta M}{M}(\%)$
	PEG-400	PEG-1000	
iso-C.H.OH-iso-C.D.OH	1.0380	1.0430	11.7
C,H,OH-C,D,OH	1.0313	1.0362	10.8
CH <sub>3</sub> COCH <sub>3</sub> -CD <sub>3</sub> COCD <sub>3</sub>	1.0324	1.0333	10.3
CH <sub>3</sub> OH-CĎ <sub>3</sub> OH	1.0228	1.0272	9.4
C5H5NC5D5N	1.0190	1.0140	6.3

### TABLE III

ratios of retentions,  $V'_{R(H)}/V'_{R(D)}$ , at 55° and differences in molecular weight (%) for some polar substances separated on PEG-400 and PEG-1000

in their interactions with polar liquid phases. In all cases, a certain correlation with the molecular weight is observed (Table III). The experimental results we have obtained on the separation of isotopic mixtures of alcohols, acetone and pyridine on PEG and PPG-1025 have lent additional support to this observation. From the value of the  $\gamma_D'\gamma_H$  ratio of the CH<sub>3</sub>OH-CD<sub>3</sub>OH pair (see Table II), it can be seen, in particular, that methanol interacts with polar solvents more strongly than deuteromethanol.

The dipole moment of methanol (1.70b) is larger than that of ethanol and isopropanol (1.68), while its polarizability (3.9) is less (5.6 and 8.4, respectively); probably because of this difference, the forces of interaction of deuteromethanol and methanol with solvents are less than those for the other pairs and hence the separation coefficient for this pair is less than that for the other systems (Fig. 5). The



Fig. 5. Temperature dependence of coefficient of separation on PPG-1025. (1)  $C_3H_7OH-C_3D_7OH$ ; (2)  $C_2H_5OH-C_2D_5OH$ ; (3)  $CH_3COCH_3-CD_3COCC_3$ ; (4)  $CH_3OH-CD_3OH$ .

better resolution of the isopropanol-deuteroisopropanol pair compared with the resolution of the ethanol-deuteroethanol system is probably due to the fact that the difference in the polarizabilities of the former system is greater than the polarizability of ethanol. It would seem that on less polar liquid phases, the polarity and polarizability of the deuterated and hydrated molecules differ even more.

The resolution of the pyridine-deuteropyridine pair on PEG, however, yielded different results. As the  $V'_{R(H)}/V'_{R(D)}$  ratio is less than unity, it follows that deuteropyridine interacts with polar solvents more strongly than pyridine. It should be noted that in this particular case the resolution is determined by the relative polarity of the liquid phase. If the polarity of acetone is compared with that of pyridine the dipole moment of acetone (2.85) is greater than that of pyridine (2.20), but for an acetone-deuteroacetone mixture the isotopic effect is a reverse one, and for a pyridine-deuteropyridine mixture it is normal. This indicates that the presence of different functional groups in the acetone and pyridine molecules influences the isotopic effect.

### REFERENCE

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