CHROM. 6277

SEPARATION OF ISOTOPICALLY SUBSTITUTED POLAR COMPOUNDS DERIVED FROM HYDROCARBONS

K. I. SAKODYNSKII, LE-CHI-LE and P. P. ALIKHANOV

Karpov Institute of Physical Chemistry, Moscow (U.S.S.R.)

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.*[1].

The present paper deals with the separation of a number of polar compounds on c·· r 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° and 4–5 atm for 5–6 h. To improve the shape of the peaks, a surface-active 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–deutero-ethanol 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 μl 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
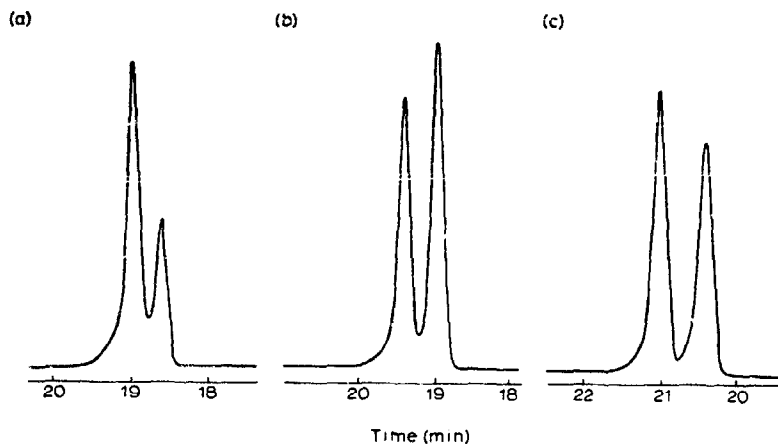

Fig. 1. Separation of C_1–C_3 alcohols on PEG-1000. (a) CH_3OH–CD_3OH, 42°, 1.1 ml/min; (b) C_2H_5OH–C_2D_5OH, 46°, 1.15 ml/min; (c) iso-C_3H_7OH–iso-C_3D_7OH, 44°, 1.1 ml/min.
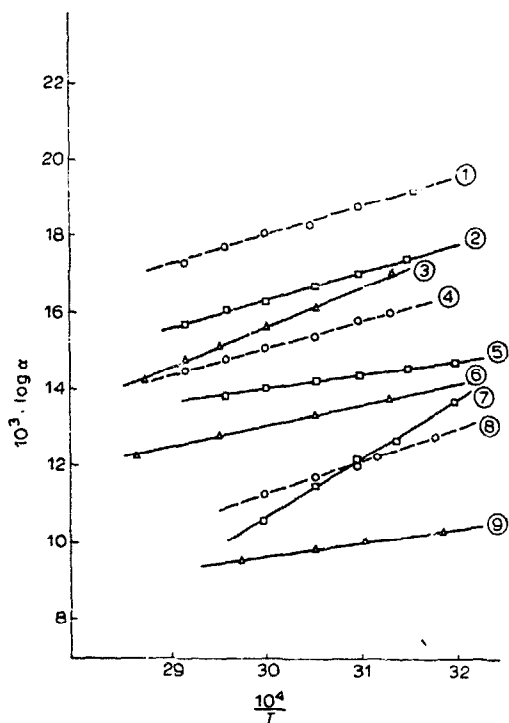

Fig. 2. Coefficient of separation for alcohols on different stationary phases. iso-C_3H_7OH–iso-C_3D_7OH on (1) PEG-1000, (2) PEG-600, (3) PEG-400; C_2H_5C C_2D_5OH on (4) PEG-1000, (5) PEG-600, (6) PEG-400; CH_3OH–CD_3OH on (7) PEG-600, (8) PEG-1000, (9) PEG-400.

pressures and retention volumes[1], the ratio of the activity coefficients, γ_D/γ_H, at different temperatures was calculated for the CH_3OH–CD_3OH 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_3OH–CD_3OH 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, γ_D/γ_H, of the CH_3OH–CD_3OH 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 first to be eluted. The resolution was found to be best on PEG-1000 and PPG-
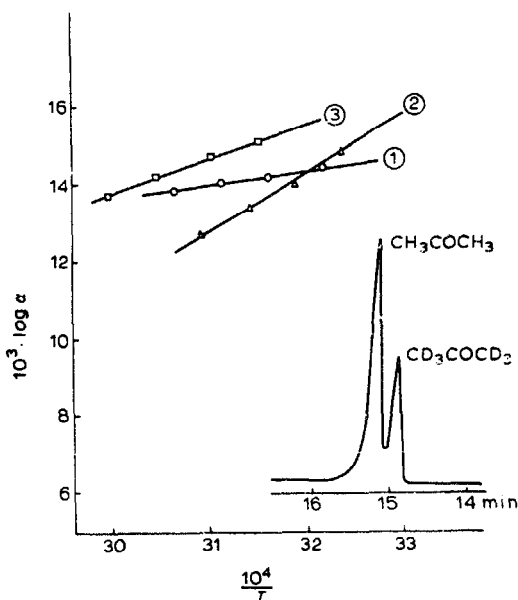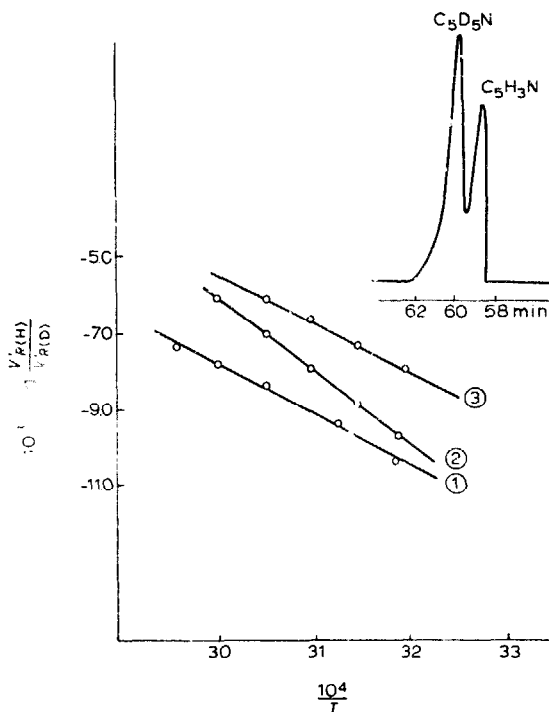

Fig. 3. Separation of acetones and temperature dependence of coefficient of separation, on (1) PEG-400, (2) PEG-600 and (3) PEG-1000.

TABLE I

DIFFERENCES IN THE ENTHALPIES (cal/mole) AND ENTROPIES (cal/mole·°C, $\times 10^2$) FOR SOME SYSTEMS ON POLAR STATIONARY PHASES

Temperature range 35–85

Mixture	Stationary phase													
	PEG-400				PEG-600				PEG-1000				PPG-1025	
	ΔH_H	ΔH_D	ΔS_H	ΔS_D	ΔH_H	ΔH_D	ΔS_H	ΔS_D	ΔH_H	ΔH_D	ΔS_H	ΔS_D	$\Delta H_H - \Delta H_D$	$\Delta S_H - \Delta S_D$
CH_3OH CD_3OH	−19.4			0.51	72.7			17.9	−40.6			6.84	−24.60	−1.00
C_2H_5OH C_2D_5OH	−24.6			1.42	15.0			1.65	−32.9			2.95	−90.51	−19.60
iso-C_3H_7OH iso-C_3D_7OH	−40.6			7.71	33.0			2.70	−34.4			2.07	−49.20	−6.00
CH_3COCH_3 CD_3COCD_3	−15.8			1.49	65.3			14.4	−49.7			5.93	−12.30	+3.70
C_5H_5N C_5D_5N	+90.7			+14.6	+90.82			+24.5	+59.36			+14.4		

TABLE II

RATIOS OF RETENTIONS $V_{R(H)}/V_{R(D)}$, VAPOUR PRESSURES, P_D/P_H, AND COEFFICIENTS OF ACTIVITY, γ_D/γ_H, FOR THE CH_3OH–CD_3OH SYSTEM

Temperature (°C)	$\dfrac{P_D}{P_H}$	Stationary phase							
		PEG-400		PEG-600		PEG-1000		PPG-1025	
		$\dfrac{V_{R(H)}}{V_{R(D)}}$	$\dfrac{\gamma_D}{\gamma_H}$	$\dfrac{V_{R(H)}}{V_{R(D)}}$	$\dfrac{\gamma_D}{\gamma_H}$	$\dfrac{V_{R(H)}}{V_{R(D)}}$	$\dfrac{\gamma_D}{\gamma_H}$	$\dfrac{V_{R(H)}}{V_{R(D)}}$	$\dfrac{\gamma_D}{\gamma_H}$
40	1.00720	—	—	1.0329	1.0246	—	—	—	—
41	1.00724	1.0240	—	—	—	1.0300	—	1.0349	1.0275
42	1.00728	—	1.0166	1.030	1.0223	—	1.0225	—	—
46	1.00744	—	—	—	—	1.0288	1.0211	1.0344	1.0268
48	1.00752	1.0232	1.0155	—	—	—	—	—	—
49	1.00756	—	—	—	—	—	—	—	—
50	1.00760	—	—	1.0284	1.0206	1.0280	1.0202	1.0337	1.0259
55	1.00780	1.0228	1.0148	1.0268	1.0188	1.0272	1.0192	1.0329	1.0249
60	1.00800	—	—	1.0250	1.0168	1.0265	1.0183	1.0326	1.0244
63	1.00812	1.0220	1.0137	—	—	—	—	—	—

1025. At temperatures below 37°, the resolution on PEG-600 was better than that on PEG-400, and above 37° 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 deutero-pyridine 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-400, (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

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

Mixture	$\dfrac{V'_{R(H)}}{V'_{R(D)}}$		$\dfrac{\Delta M}{M}$ (%)
	PEG-400	PEG-1000	
iso-C_3H_7OH–iso-C_3D_7OH	1.0380	1.0430	11.7
C_2H_5OH–C_2D_5OH	1.0313	1.0362	10.8
CH_3COCH_3–CD_3COCD_3	1.0324	1.0333	10.3
CH_3OH–CD_3OH	1.0228	1.0272	9.4
C_5H_5N–C_5D_5N	1.0190	1.0140	6.3

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_3OH–CD_3OH 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 (1.706) 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
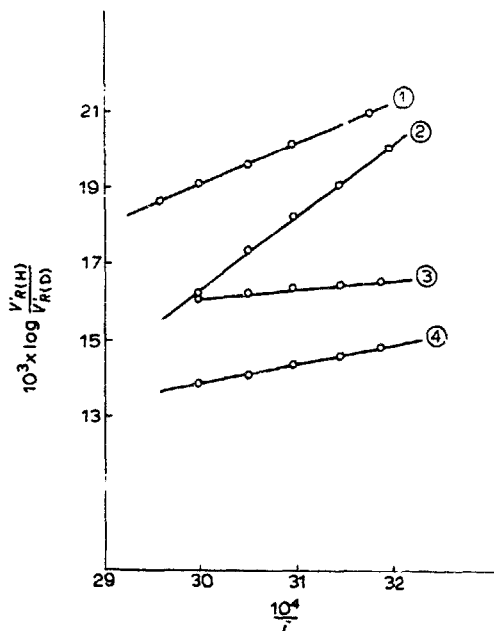

Fig. 5. Temperature dependence of coefficient of separation on PPG-1025. (1) C_3H_7OH–C_3D_7OH; (2) C_2H_5OH–C_2D_5OH; (3) CH_3COCH_3–CD_3COCD_3; (4) CH_3OH–CD_3OH.

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

1 G. P. CARTONI, A. LIBERTI AND A. PELA, *Anal. Chem.*, 39 (1967) 1618.