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THE EFFECT OF ELECTROLYTES IN THE STATIONARY PHASE ON GAS-LIQUID CHROMATOGRAPHIC ELUTION*,**

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SUMMARY

To determine the effects exerted on the gas chromatographic elution of many aliphatic and aromatic compounds by the electrolytes LiCl, CsCl, KCl and KOH dissolved in the stationary phase (Carbowax 400), the authors compared the retention volumes obtained in the presence and absence of electrolytes in the stationary phase, and calculated the change in the partial molar free energy $\Delta G^0_{t,1 \rightarrow 2}$ accompanying the transfer of one mole of a solute from one stationary phase to the other. While the electrolytes did not differ appreciably from one another, the solutes differed considerably in their behaviour. Aliphatic hydrocarbons showed a stronger salting-out effect than aromatic ones. While primary alcohols exhibited a considerable salting-in effect, tertiary ones showed a salting-out effect, the behaviour of secondary ones being intermediate. The experimental results may find applications in analysis.

INTRODUCTION

It is well known that the properties of some stationary phases may be modified by the addition of electrolytes. BRADFORD *et al.*¹ have used silver nitrate dissolved in glycol for the analysis of olefinic compounds. Many other authors^{2,3} have made wide use of methods of this kind with different solutes and stationary phases. The choice of this electrolyte was influenced by the possibility of a complex formation between the Ag⁺ ion and the samples. The selectivity of the stationary phases was found to be dependent on the stability constants of the adducts, and in some cases the gas chromatographic method has in fact been used to determine these constants⁴. BANTHORPE *et al.*⁵ have proposed the replacement of silver nitrate by thallium nitrate for the analysis of olefinic and aromatic compounds. The possibility of a specific interaction between solute and cations in the stationary phase has been extensively discussed by other authors⁶⁻¹⁰.

We have recently shown the effect of LiCl in polyethyleneglycol on the retention

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of some compounds¹¹. It is known that the solubility of a non-electrolyte in solvents may change when the latter contain electrolytes¹², owing to the new interactions which may take place in such solutions¹³. The present aim was to compare the properties of Carbowax 400 (polyethyleneglycol) with and without a dissolved electrolyte (LiCl, KCl, CsCl, or KOH) during its use as a stationary phase in the elution of alkanes, aromatic hydrocarbons, and alcohols. The rate of migration of a volatile solute through a GLC column is expressed by the specific retention volume V_g (Ref. 14). This parameter can be correlated with the partition coefficient¹⁵ by the equation:

$$V_{gA,1} = \frac{273}{T_c} K_{A,1} \quad (1)$$

where: $V_{gA,1}$ is the specific retention volume of compound A in phase 1, T_c is the column temperature ($^{\circ}\text{K}$), and $K_{A,1}$ is the partition coefficient, expressed as weight of solute per gram of stationary phase, divided by the weight of solute per ml of gas at the column temperature (concentrations are substituted for activities). $K_{A,1}$ may be considered to be the equilibrium constant for the transfer of solute A from the gas phase to solution¹⁶. The equation

$$\Delta G^0_1 = -RT_c \ln K_{A,1} \quad (2)$$

therefore expresses the change in free energy in the process of transferring one mole of component A from the gas phase into solution, when the ml/g ratio of the concentrations is the unit. Considering the same solute A in phase 2, we can write:

$$V_{gA,2} = \frac{273}{T_c} K_{A,2} \quad (3)$$

where the symbols have the same values as above, but refer to solute A in phase 2. Moreover,

$$\Delta G^0_2 = -RT_c \ln K_{A,2} \quad (4)$$

and so it can be shown that¹⁷:

$$\Delta G^0_{t,1 \rightarrow 2} = RT_c \ln \frac{K_{A,1}}{K_{A,2}} \quad (5)$$

where $\Delta G^0_{t,1 \rightarrow 2}$ is the free energy of transfer of one mole of solute A from phase 1 to phase 2 when the concentrations in the two phases are equal. It follows from eqns. 1 and 3 that

$$\Delta G^0_{t,1 \rightarrow 2} = RT_c \ln \frac{V_{gA,1}}{V_{gA,2}} \quad (6)$$

When Carbowax 400 without an electrolyte is called stationary phase 1 and Carbowax 400 containing a dissolved electrolyte is called phase 2, a negative value of $\Delta G^0_{t,1 \rightarrow 2}$ indicates salting-in ($V_{gA,2} > V_{gA,1}$), while a positive value indicates salting-out ($V_{gA,2} < V_{gA,1}$). Furthermore, it is profitable to correlate the salting effect

with the salt concentration in the stationary phase. The following expression, which is similar to Setschenow's equation, can be used for this purpose:

$$\Delta G_{t,1 \rightarrow 2}^0 = RT_c \ln \frac{V_{g\Lambda,1}}{V_{g\Lambda,2}} = K m \quad (7)$$

Constant K is a measure of the effect of adding an electrolyte to the stationary phase in a hypothetical $1 m$ concentration.

Experimental

The apparatus used for the gas chromatographic measurements was a Fractovap GV Model 200 (C. Erba, Milan), fitted with a thermal detector. Steel columns with a length of 1–2 m and an internal diameter of 6 mm were used. The carrier gas was helium, the flow rate being about 1 ml/sec (for 0°C and 760 mm Hg). The stationary phase was Carbowax 400 (Cw 400) (C. Erba), and the electrolytes were high-purity products (Merck, Darmstadt). The support was 60–80 mesh silanized Chromosorb P (C. Erba). Tests carried out at 25°C showed that 1000 g of Cw 400 (product made for GLC and used without further purification) dissolved about 0.8 mole of LiCl, 0.15 mole of KCl, and 0.4 mole of CsCl. The column was prepared by evaporating a methanolic solution of the electrolyte and Cw 400 on the support. The amount of the stationary phase was 20 % of the weight of the support. The concentration of the electrolyte in the stationary phase was expressed in molality. All measurements were made at a temperature of 78°C.

In order to make a significant comparison, columns containing LiCl and CsCl were investigated in the same range of concentrations, the limits of which were set by the low solubility of CsCl (at 25°C) and the need to observe measurable changes in V_g . We also studied the effect of KOH, whose concentrations in Cw 400 (0.327 m and 0.487 m) were below the solubility limit. KCl was studied only qualitatively, owing to its low solubility in Cw 400 (excessively small amounts of electrolyte cause insufficient changes in V_g and thus the determination of $\Delta G_{t,1 \rightarrow 2}^0$ involves a great error). However, the retention volumes obtained on columns containing only a small quantity of KCl (ca. 0.1 m) showed that this electrolyte had qualitatively the same effect as CsCl, LiCl and KOH. The effect of the electrolytes on the retention of the various solutes was expressed with the aid of constant K of eqn. 7, as a mean of two or more concentrations. In the concentration range considered, this equation gives a satisfactory expression of the variation of $\Delta G_{t,1 \rightarrow 2}^0$ with the concentration of the electrolyte.

It should be stressed that the thermodynamic quantities used to express the experimental results are closely connected with the nature of the gas–liquid equilibrium system used¹⁸. Adsorption phenomena at the gas–liquid interface¹⁹, which may be modified by the electrolyte, can influence the establishment of this equilibrium. A second limitation, which must always be considered when interpreting the experimental data, is the particularly complex nature of solutions of electrolytes in solvents having a low dielectric constant²⁰. According to the type of electrolyte, these solutions may exhibit phenomena of association between ions or dissolution of micelles composed of a number of molecules. For these reasons, it does not seem to be possible to interpret the differences in behaviour between the various electrolytes. The tailing was the same whether or not the stationary phase contained an electrolyte.

RESULTS AND DISCUSSION

The data in Table I illustrate the typical effects of electrolytes on the elution of some compounds, these particular data having been obtained with 0.309 *m* of CsCl at 78°C. All hydrocarbons show a salting-out effect, which is highest for aliphatic compounds. Alcohols, on the other hand, exhibit a salting-in effect. The results obtained with LiCl were similar¹¹. This behaviour suggests a general interpretation: It appears that electrolytes increase the polarity of the stationary phase, as the retention of non-polar and non-polarizable compounds is considerably lower in their presence (this reduction being less marked with solutes containing a dipole, π -electrons, or halogens). The increase in the retention volume of alcohols, occurring by an increase in their solubility in the stationary phase when an electrolyte is added, can be correlated with the type of specific interactions (hydrogen bonding) between alcohols and the stationary phase²¹.

We shall now discuss in detail the effects on the elution of various classes of compounds.

TABLE I

THE EFFECT OF THE ADDITION OF CsCl TO CARBOWAX 400 ON THE RETENTION VOLUMES OF VARIOUS COMPOUNDS

	$V_{g\ A,1}$ (Cw 400)	$V_{g\ A,2}$ (Cw 400 + 0.309 <i>m</i> CsCl)	$\frac{V_{g\ A,1}}{V_{g\ A,2}}$
<i>n</i> -Decane	76.1	60.9	1.25
Carbon tetrachloride	42.4	38.3	1.11
Benzene	68.9	64.2	1.07
2-Propanol	99.1	103.8	0.95
1-Propanol	200	218	0.92

Hydrocarbons and halogen derivatives

The values of the constant *K* are shown in Table II. It can be seen that the effect produced by KOH is weaker than that produced by the other electrolytes. In general, cyclohexane and CCl₄ exhibit a weaker salting-out effect than aliphatic hydrocarbons. For the latter, the value of *K* increases slightly from *n*-hexane to *n*-decane only in the presence of CsCl. The comparison of benzene, toluene, and chlorobenzene is interesting: there is stronger salting-out with toluene than with benzene and chlorobenzene.

The effect of substituents in the aromatic nucleus was extensively studied at a high concentration of LiCl (0.766 *m*) in order to exaggerate the changes in retention volume. The results in Table III show that methyl groups in the ring have a salting-out effect and halogens have a salting-in effect with respect to benzene. The results obtained for an *n*-alkane (*n*-decane) and thiophen are shown in the same table for comparison. The last column shows the values of the excess partial molar free energy ($\Delta\mu^E$) determined before^{21,22} in pure Cw 400 at 78°C. These values reflect the thermodynamic behaviour in pure Cw 400, and are seen to run parallel to $V_{g\ A,1}/V_{g\ A,2}$ in the case of aromatic compounds and thiophen. In the presence of electrolytes, substituents which cause a positive (or negative) deviation from Raoult's law in pure

TABLE II

VALUES OF THE CONSTANT K FOR HYDROCARBONS AND HALOGEN DERIVATIVESThe constant K is the free energy of transfer at 78°C at a hypothetical 1 m concentration (kcal/mole).

	LiCl ^a	CsCl ^b	KOH ^c
<i>n</i> -Hexane	0.42	0.46	0.21
<i>n</i> -Heptane	0.43	0.47	0.21
<i>n</i> -Octane	0.45	0.47	0.21
<i>n</i> -Nonane	0.43	0.49	0.18
<i>n</i> -Decane	0.45	0.53	0.18
Cyclohexane	0.37	0.40	0.19
Carbon tetrachloride	0.26	0.23	0.17
Benzene	0.22	0.18	0.15
Toluene	0.26	0.24	0.17
Chlorobenzene	0.19	0.14	0.13

^a Mean of the molal concentrations: 0.327, 0.348, 0.458.^b Mean of the molal concentrations: 0.230, 0.309.^c Mean of the molal concentrations: 0.327, 0.487.

TABLE III

THE EFFECT OF SUBSTITUENTS IN THE BENZENE RING ON RETENTION VOLUMES AND THE EXCESS PARTIAL MOLAL FREE ENERGIES

	$V_{gA,1}$ (Cw 400, 78°C)	$V_{gA,2}$ (0.766 m LiCl, 78°C)	$\frac{V_{gA,1}}{V_{gA,2}}$	$\Delta \mu^E$ (kcal/mole, 78°C)
<i>p</i> -Xylene	225	159.4	1.41	+0.37
<i>m</i> -Xylene	234	165.8	1.41	+0.37
<i>o</i> -Xylene	310	222	1.40	+0.30
Toluene	127.4	94.4	1.35	+0.13
Benzene	68.9	53.1	1.30	-0.11
Chlorobenzene	375	294	1.28	-0.15
Fluorobenzene	89.8	70.0	1.28	-0.20
Thiophen	115.5	92.5	1.25	-0.39
Carbon tetrachloride	42.4	32.2	1.32	+0.15
<i>n</i> -Decane	76.1	47.8	1.59	+2.08

Cw 400 lead to a stronger (or weaker) salting-out effect in comparison with benzene. This is also found by comparing aliphatic hydrocarbons with CCl₄ and aromatic hydrocarbons.

Alcohols

The following conclusions can be drawn from the data in Table IV: (1) The solubility of primary alcohols increases in the presence of any of the electrolytes in the stationary phase. The salting-in effect decreases with increasing chain length. (2) The secondary alcohol (2-propanol) exhibits a weaker salting-in than the corresponding primary alcohol.

With KOH, the salting-in effect is consistently weaker, and 2-propanol exhibits slight salting-out. These observations have been confirmed by the examination of more alcohols. The results obtained with 0.487 m KOH at 78°C are reported as an example in Table V. The behaviour of the other electrolytes (LiCl and CsCl) was

TABLE IV

VALUES FOR THE CONSTANT K FOR ALCOHOLSThe constant K is the free energy of transfer at 78°C at a hypothetical 1 *m* concentration (kcal/mole).

	$LiCl^a$	$CsCl^b$	KOH^c
Methanol	-0.39	-0.37	-0.27
Ethanol	-0.24	-0.25	-0.11
1-Propanol	-0.14	-0.18	-0.10
2-Propanol	-0.06	-0.10	+0.05

^a Mean of the molal concentrations: 0.327, 0.348, 0.458.^b Mean of the molal concentrations: 0.230, 0.309.^c Mean of the molal concentrations: 0.327, 0.487.

TABLE V

THE EFFECT OF THE ADDITION OF KOH TO CARBOWAX 400 ON RETENTION VOLUMES OF ALCOHOLS

	$V_{R \Lambda, 1}$ (Cw 400, 78°C)	$V_{R \Lambda, 2}$ (0.487 <i>m</i> KOH, 78°C)	$\frac{V_{R \Lambda, 1}}{V_{R \Lambda, 2}}$	pK_a^*
Methanol	83.5	101.7	0.82	16
Ethanol	105.8	115.1	0.92	16.62
1-Propanol	200	213	0.94	—
2-Propanol	99.1	96.4	1.03	—
1-Butanol	389	401	0.97	16.82
2-Butanol	178.2	169.9	1.05	17.20
2-Methylpropanol-2	82.3	75.0	1.10	17.62
2-Methylbutanol-2	162.3	145.9	1.11	—

* Data reported by DIERCKX *et al.*²⁶.

qualitatively very similar. In addition to what has been already stated, tertiary alcohols have a stronger salting-out effect than secondary alcohols.

The great increase in solubility, a characteristic mainly of primary alcohols, cannot be explained on the basis of their high dipole moment (1.6–1.7 *D*) alone. In fact, it has already been observed that other substances with a similar dipole moment (chlorobenzene and fluorobenzene) have a salting-out effect. By contrast, the increase in the solubility of alcohols may be connected with the electrostatic character of the bond which they form with pure Cw 400. The differences in behaviour between primary, secondary, and tertiary alcohols follow the progressive decrease in the electrostatic contribution of the hydrogen bond when these alcohols behave as proton donors^{23–24}. The isomerization of the carbon chain leads to a higher inductive effect, with an increased electron density on the hydroxyl group²⁵. The parallel between the acid strength (pK_a) and the salt effect is illustrated by the case of the three butanols in Table V, but it has been found with primary alcohols as well.

The above results show that the characteristics of the stationary phase can be modified by the addition of electrolytes. Thus, the retention volume of a compound depends not only on its nature but also on the amount of added electrolyte.

Fig. 1 shows one example of the use of these effects in the separation of methanol and *tert.*-butanol. Although pure Cw 400 was unable to separate a mixture of these two compounds, Cw 400 + 0.487 *m* of KOH gave a good separation under the same

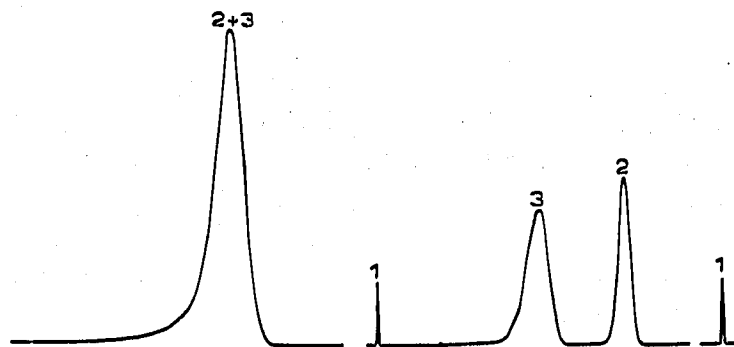


Fig. 1. Chromatograms for a mixture of methanol (3) and 2-methylpropanol-2 (2). Left: Carbowax 400, right: Carbowax 400 + 0.487 *m* KOH. The operating conditions are described in the experimental part. Column: 2 m, I.D. 6 mm.

conditions. The elution of methanol (a primary alcohol) is slowed down in the presence of the electrolyte, whereas the elution of 2-methylpropanol-2 (a tertiary alcohol) is accelerated. Other similar mixtures of alcohols may be resolved in the same way because these properties are quite general. The effect of the addition of electrolytes to the stationary phase is manifested also beyond the solubility limits previously mentioned. On such columns, the changes in solubility are more marked, and they are therefore more efficient for analytical purposes.

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