THE USE OF GAS–LIQUID CHROMATOGRAPHY FOR SELECTING EXTRACTIVE SOLVENTS FOR LIQUID EXTRACTION PROCESSES

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SUMMARY

Gas–liquid chromatography is used for the selectivity determination of various solvents.

The group selectivity of 28 solvents in the separation of cyclic and aliphatic sulfides from the hydrocarbons is investigated. The solvents containing –OH and –NH$_2$ groups were found to be the most selective in separating the cyclic sulfides and monocyclic aromatic hydrocarbons.

The data obtained allowed an extractive solvent (phenol) to be chosen for separating the cyclic sulfides from the kerosene-gas-oil fractions.

With the straight-run petroleum fraction 275–350° the possibility of obtaining the sulfide concentrates with the help of liquid extraction is experimentally confirmed.

Recently, gas–liquid chromatography has been widely used for the determination of thermodynamic functions of solutions, the limiting values of activity coefficients and solvent selectivities[1,2]. This method is characterized by a good reproducibility of results, rapid analyses and very small consumptions of reagents.

We used gas–liquid chromatography for the selection of solvents that would enable cyclic sulphides (thiophanes) to be separated from their mixtures with hydrocarbons. Data available from the literature do not allow the possibility of performing such separations to be judged[3–7]. Moreover, it is considered that the sulphur compounds contained in oil fractions cannot be separated from aromatic hydrocarbons[8] by any solvent except aqueous sulphuric acid. The extraction process with sulphuric acid has been described in detail[8,9].

The results obtained may have practical importance as the sulphide concentrates and the sulphoxides produced by such methods may find extensive use as flotation agents, extraction agents for isolating and separating some metals and for other purposes[10].

The value of group selectivity for the separation of sulphur compounds and hydrocarbons was expressed by the logarithm of a limiting separation coefficient ($\log \beta^0_{s-h}$):

$$\log \beta^0_{s-h} = \log \frac{\gamma^0_h}{\gamma^0_s} \tag{1}$$

where γ^0_h and γ^0_s are the limiting activity coefficients of the hydrocarbon and sulphur compounds, respectively, in the solvent investigated.

TABLE I

THE SELECTIVITY OF SOLVENTS IN THE SEPARATION OF SULPHUR COMPOUNDS AND HYDROCARBONS AT 50°

Solvents	Diisopropyl sulphide– n-octane	Thiophane– n-octane	2-Methyl- thiophene– n-octane	Diisopropyl sulphide– toluene	Thiophane– toluene	2-Methyl- thiophene– toluene	Toluene– n-heptane
Phenol and its derivatives							
Phenol	1.10	1.44	0.95	0.29	0.64	0.15	0.73
o-Cresol	0.91	1.23	0.80	0.22	0.55	0.12	0.51
m-Cresol	0.87	1.14	0.78	0.21	0.48	0.12	0.59
p-Cresol	0.87	1.15	0.77	0.22	0.50	0.12	0.59
o-Chlorophenol	0.80	1.05	0.73	0.16	0.41	0.09	0.53
Alcohols and glycols							
Ethylene glycol	0.58	1.20	1.05	0.26[a]	0.35	0.20	1.24
Triethylene glycol	0.78	1.33	1.40	0.42[a]	0.13	0.20	1.04
Benzyl alcohol	0.68	1.02	0.88	0.055[a]	0.29	0.14	0.64
Furfuryl alcohol	0.91	1.35	1.21	0.14[a]	0.30	0.16	0.94
Esters							
Propylene carbonate	0.86	1.25	1.36	0.36[a]	0.04	0.15	1.12
Dimethyl malonate	0.67	0.93	1.06	0.27[a]	0.01[a]	0.12	0.84
Diethyl oxalate	0.65	0.90	0.93	0.18[a]	0.07	0.10	0.55
Diisopropyl malonate	0.48	0.62	0.73	0.16[a]	0.01[a]	0.09	0.55
Nitrogen-containing compounds							
Formamide	0.87	1.66	1.44	3.34[a]	0.45	0.23	1.06
Ethyl carbamate	0.79	1.11	1.06	0.15[a]	0.18	0.13	0.82
Aniline	0.82	1.26	1.09	0.08[a]	0.30	0.19	0.87
Dimethylaniline	0.57	0.78	0.80	0.12[a]	0.09	0.11	0.53
Nitrobenzene	0.55	0.77	0.82	0.10[a]	0.07	0.11	0.66
Benzonitrile	0.58	0.79	0.84	0.15[a]	0.06	0.11	0.68
1-Nitro-2-methylpropanol-2	0.78	1.16	—	0.21	0.20	—	0.87
N-Methylpyrrolidone	0.68	1.01	1.22	0.38[a]	0.05[a]	0.17	0.94
Sulphur-containing compounds							
Dimethyl sulphoxide	0.84	1.36	1.48	0.42[a]	0.09[a]	0.21	1.11
Sulpholane	0.96	1.51	1.64	0.49[a]	0.06[a]	0.19	1.31
Acetylthiophene	0.62	0.96	0.99	0.23[a]	0.11	0.14	0.80
Miscellaneous							
Furfural	0.67	1.03	1.04	0.21[a]	0.14	0.16	0.89
Maleic anhydride	1.05	1.01	1.70	0.47[a]	0.10	0.18	1.41
n-Tetradecane	0.02[b]	0.10[a]	0.01[a]	0.01[a]	0.09[a]	0.001[a]	0.03[b]
α-Methylnaphthalene	0.34	0.51	0.49	0.05[a]	0.12	0.10	0.37

[a] The hydrocarbon is a readily soluble component.
[b] Heptane is a readily soluble component.

The ratio of the activity coefficients was determined by gas–liquid chromatography in terms of the expression:

$$\frac{\gamma^0_h}{\gamma^0_s} = \frac{V_s \cdot P_s}{V_h \cdot P_h} \tag{2}$$

where V and P are the retention volumes on the stationary phase and the vapour pressure of the compounds separated (sulphur compounds and hydrocarbons), respectively, at the temperature of experiment.

The experiments were performed on a Fractovap D chromatograph obtained from Carlo Erba, Milan. The inert support (silanized Chromosorb G, 100–120 mesh) was coated with the solvents studied, which served as stationary liquid phases. The ratio of the liquid phase to the inert support was 10% by weight. We used micropacked glass columns, 2 m long and I.D. 1.5 mm. The work was carried out under isothermal conditions at 50°.

Most of the solvents investigated have high vapour pressures. Therefore, in order to prevent solvent losses, the carrier gas was passed through a saturator filled with the supported material impregnated with the solvent being studied.

To eliminate the drift of the baseline owing to the high volatility of the solvents, a dual-column system was used.

Very small samples (up to 0.01 μl) were used so as to carry out the solution process under the optimum conditions of infinite dilution, which was readily effected by using a highly sensitive flame ionization detector.

The selectivities of 28 solvents for different types of compounds, including 10 solvents used in the petroleum industry and 2 hydrocarbons, were determined. The results are shown in Table I. For comparison, the selectivities of toluene and heptane are also given.

The results obtained show that virtually all of the solvents studied possess a sufficiently high selectivity for the separation of the sulphur compounds and paraffins indicated. With thiophane and 2-methylthiophene, the selectivity is even higher than that in separation of alkylbenzenes and paraffins.

The selectivity of the solvents investigated in the separation of 2-methylthiophene and toluene is small. The most selective compounds are formamide (0.23) and dimethyl sulphoxide.

We developed an equation correlating the selectivity of the separation of 2-methylthiophene (2MT) and n-heptane (H) with that of toluene (T) and n-heptane, of the form

$$\log \beta^0_{2MT-H} = \alpha \log \beta^0_{T-H} \tag{3}$$

From this equation, it follows that the coefficient α may be considered as being a relative selectivity. In the present instance, $\alpha = 1.171$. The accuracy of this correlation is characterized by the following: the quadratic mean deviation of a single measurement is 2.3%, the maximum deviation is 4.6% and the correlation coefficient is 1.000.

The high accuracy of this correlation naturally does not guarantee that there may be a solvent that is significantly different from the one considered here; however, high deviations are unlikely.

The selectivity in the separation of thiophane from toluene is generally dependent on the nature of the solvent. For most of the solvents investigated the selectivity is small. Only the compounds containing –OH and –NH$_2$ groups have relatively high selectivities (the maximum for phenol, 0.64).

The phenol selectivity is sufficiently high to separate sulphide concentrates from oil fractions boiling in the range 50–100°. This assumption was confirmed experimentally. By using liquid extraction, we obtained concentrates containing up to 60–70% of sulphides from a straight-run petroleum fraction of boiling range 275–350°.

In the separation of toluene and diisopropyl sulphide, the aromatic hydrocarbon is a readily soluble component.

In the separation of thiophane and toluene, *n*-paraffins (*n*-tetradecane) preferentially elute toluene. This indicates that reflux in the extraction system on the side of the extraction solution exit has to be reasonably disturbed by supplying a counter-solvent.

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