Joanna Masłowska, Krystyna Nowicka

OPTIMIZATION OF CHROMATOGRAPHIC SEPARATION OF SOLVENT MIXTURE BASED ON THERMODYNAMIC FUNCTIONS OF ADSORPTION AND DISSOLUTION

Based on determined specific retention volumes for components of solvent mixture, their heats of adsorption ($-\Delta H$) on a chromosorb W AW DMCS (80-100) mesh support and heats of dissolution ($-\Delta H$) on partition packing with various contents of stationary liquid phase OV-101 (from 3 to 17 % by wt.) were calculated. On the basis of the found values of heat of adsorption, it was found that chromosorb W AW DMCS is a suitable support for the separation of solvent mixture. The optimal content of liquid phase, at which adsorption effects at the interface of stationary liquid phase (OV-101) carrier gas (argon) are minimal, was found to be 10 % by wt. Using n-hexane and n-heptane as standard substances, the retention indices (I_x) of the investigated solvents on a column filled with 10 % OV-101 on chromosorb W AW DMCS at a temperature of 353 K were determined.

Such solvents as n-butyl alcohol, n-butyl acetate, methyl isobutyl ketone, methyl ethyl ketone, xylene, petroleum spirits and solvent naphtha are commonly used in many branches of industry. The two latter of the mentioned solvents are complex mixtures of aliphatic, anphthenic and aromatic hydrocarbons. The mixture of solvents is used in the manufacture of paints and lacquers, and mainly chlorinated rubber and epoxyde paints. These solvents are toxic substances, and therefore, there is necessity for permanent control of their concentration in air in the works where they are used. A method for the determination of the mentioned solvent mixture in air has not yet been reported. Known are only chromatographic methods for the determination of

individual solvents [1-3] or simple mixtures of two or three components [4-8].

The aim of the present study was to find conditions for the chromatographic separation of complex mixture which could also be useful in the determination of simple solvents (n-butyl, alcohol, n-butyl acetate, methyl ethyl ketone, methyl isobutyl ketone and xylene) in the presence of complex solvents: solvent naphtha and petroleum spirits. To achieve this aim, gas chromatography with typical columns containing partittion packing was applied. Experiments were planned to select a suitable support, stationary liquid phase and optimal amount of liquid phase at which adsorption phenomens at the interfase: stationary liquid - carrier gas, able to affect the retention data, could be reduce to minimum.

Experimental

Chemicals

- n-butyl alcohol, n-butyl acetate and xylene, all of them of analytical grade supplied by POCh - Gliwice (Poland).
- methyl ethyl ketone, analytical grade (Reanal, Hungary).
- methyl isobutyl ketone, analytical grade (Merck, GFR).
- petroleum spirits and solvent naphtha (Petrochemical Rafinery, Gdańsk, Płock, Poland).
- chromosorb W AW DMCS, 80-100 mesh (Johns - Manville , USA).
- available stationary liquid phases of various polarity.

Apparaturs

- Gas Chromatograph, type N-503 (Mera Elmat, Wrocław, Poland), with a flame ionization detector.
- Microsyringes , 1 mm^3 and 10 mm^3 in volume (Hamilton).

Results and Discussion

Because of the physico-chemical properties of the investigated solvents, their separation was performed by partition chromatography using conventional chromatographic columns (3 m in length, 4 mm in inner diameter) . The stationary liquid phases under investigation were applied on chromosorb W AW DMCS, 80-100 mesh, in suitable solvents which were evaporated in a vacuum evaporator on agitation.

In partition chromatography, the values of the retention data can be also affected, besides the dissolution (partition) process, by adsorption phenomena taking place at the interface: stationary liquid phase (liquid) - support (solid) and carrier gas (gas) - stationary liquid phase (liquid)[9-13]. Interfacial adsorption brings about undesirable chromatographic band broadening, broadening of the spectral descending line, and variation of retention times with the sample size. These phenomena become of particular importance in the case of small amount of liquid phase on support or when the support is not uniformly covered by the phase or if the support is not properly selected. The extent of adsorption at the interface of stationary liquid - carrier gas is decreased with increase in the liquid phase. Therefore, in determining the parameters of chromatographic separation one should find out at what amount of liquid phase dissolution takes place on the discussed adsorption phenomena are reduced to minimum.

Many authors characterize the chromatographic column packing by finding heats of adsorption for the investigated compounds in the case of adsorption chromatography or heats of dissolution in the case of partition chromatography [14-19] .

In the first stage of the study, the usability of Chromosorb W AW DMCS was examined. So, the chromatographic column was filled with the support itself. At a given and constant temperature, into the column was introduced 1 mm^3 of the investigated substance five times and the retention times were measurred. The measurements were carried out within the temperature range 343 - 433 K. Based on the results, specific retention volumes [V_g]were

calculated, using the following formula:

$$V_g = \frac{t_R^s}{m} \cdot P_{pom} \cdot \frac{P_{pom}}{P_c} \frac{T_c}{T_{pom}} \cdot \frac{3}{2} \cdot \frac{\left(\frac{P_1}{P_0}\right)^2 - 1}{\left(\frac{P_1}{P_0}\right)^3 - 1} \qquad (1)$$

where : t_R^s - reduced retention time (min)

   m   - mass of adsorbent or liquid phase (g)

   P_{pom}- volume velocity of carrier gas (cm^3/ min)

   T_{pom}- measurement temperature(K)

   T_c - column temperature (K)

   P_{pom}- measurement pressure (Pa)

   P_c - pressure in the column (Pa)

   P_1 - gas pressure at the inlet of column (Pa)

   P_0 - gas pressure at the outlet of column (Pa)

Then, using the Clausius-Clapeyron equation, adsorption heats were found from the obtained chromatographic data. To this end, plots of log (V_g/T) vs. 1/T ·10^3 were made for each solvent, and tangents of angles were calculated by the method of least squares. Based of the results, heats of adsorption (-ΔH) were calculated according to formula (2):

$$- \Delta H = \text{tg}\alpha \cdot 2.303 \cdot R \qquad (2)$$

where: R - gas constant (J/mol K).

The values of adsorption heat for the investigated solvents on Chromosorb W AW DMCS, 80-100 mesh, are given Table 1.

Table 1. Heats of adsorption ($-\Delta H$) of the studied solvents on Chromosorb W AW DMCS (80-100 mesh).

No	Solvent	Heat of adsorption (kJ/mol)
1.	Methyl ethyl ketone	4.84
2.	n-butyl alcohol	4.76
3.	Methyl isobutyl ketone	4.64
4.	n-butyl acetate	5.14
5.	p(m)-xylene	4.71
6.	o-xylene	4.76

The values are low and similar for the six investigated solvents. They prove the physical adsorption to be low. Hence, it can be assumed that the adsorption phenomena on the support surface under the conditions investigated, will not affect the retention data. So, the Chromosorb W AW DMCS used can be considered suitable support for the studies. Next, the experiments of separation of the solvent mixture under investigation were carried out, using stationary liquid phases: SE-30; LAC-3-R--728; FFAP; Carbowax 20 M; OV-101; OV-17 with various polarities, in amounts of 10 % by wt. in relation to Chromosorb W AW DMCS (80-100 mesh). The aim was to select such a column packing which would allow to determine simple solvents (n-butyl alcohol, n-butyl acetate, methyl ethyl ketone, and methyl isobutyl ketone) in the presence of complex solvents (solvent naphtha and petroleum spirits) whose composition may be different depending on the source of crude oil. It resulted from the experiments that the most suitable one was silicone resin OV-101 which was used in further studies.

Because of the fact that during separation of the investigated compounds, adsorption phenomena can take place at the interface of liquid - carrier gas, which can be reduced to minimum by applying proper amount of liquid phase into the support , in the next stage of the study, the values of dissolution heat ($-\Delta H$) of the tested substances were examined versus the amount of stationary liquid phase on the support. From 3 to 17 % by wt. (in relation to the packing mass) of Chromosorb W AW DMCS was applied outo OV-101 silicone resin. Then, the values of specific retention volume of the investigated simple
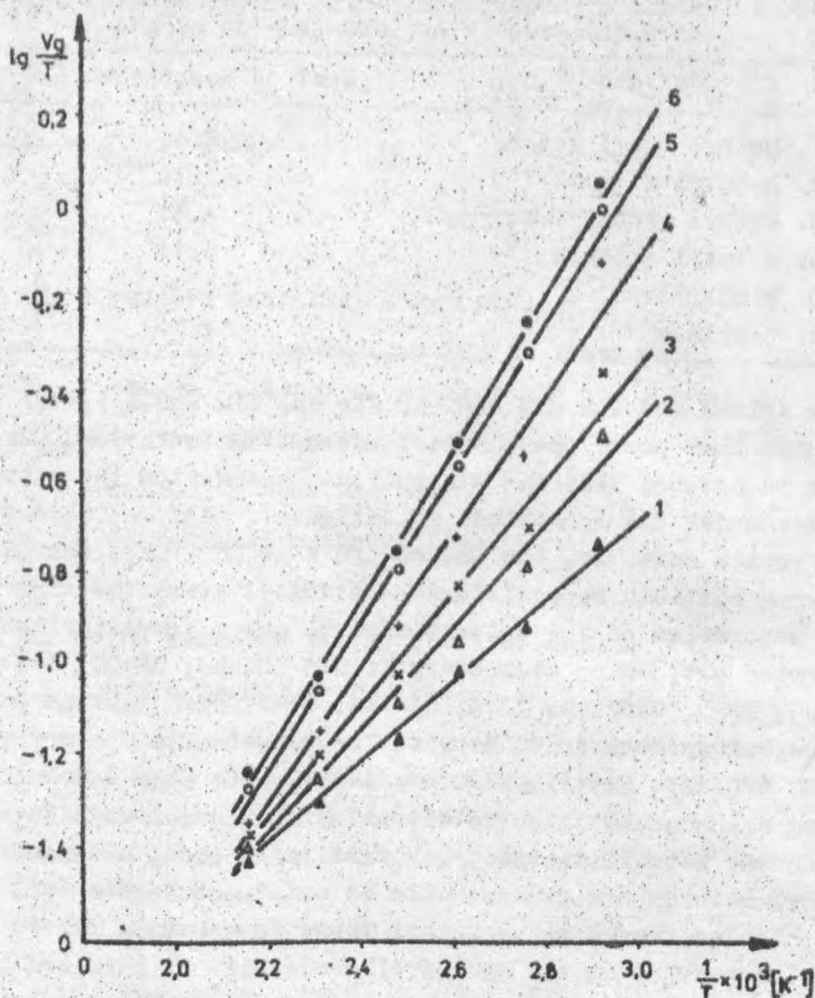
Fig. 1. Relationship between specific retention volume V_g and
        temperature of column filled up with 7 % OV-101 on
        Chromosorb W AW DMCS for the following compounds : 1 -
        methyl ethyl ketone; 2 - n-butyl alcohol; 3 - methyl
        isobutyl ketone; 4 - n-butyl acetate; 5 - p-/m/-xylene;
        6 - o-xylene.

solvents were found within the temperature range of the column
operation 343-433 K, using formula (1).Next, for each compound
on a given packing, relations of log (V_g/T) vs. $1/T \cdot 10^3$ were
plotted. Their examples are given in Fig. 1. The tangents of
inclination angles of the obtained straight lines were used to

find the values of dissolution heat ($-\Delta H$) according to formula (2). The results are given in Table 2.

Table 2. Heats of dissolution ($-\Delta H$) of the studied compounds in silicone oil OV-101 deposited on Chromosorb W AW DMCS (80-100 mesh).

No	Solvent	Heat of dissolution ($-\Delta H$)on the packing with various amounts of liquid phase OV - 101					
		3%	5%	7%	10%	13%	17%
		(kJ/mol)					
1.	Methyl ethyl ketone	12.34	13.98	15.44	16.80	18.67	18.00
2.	n-butyl alcohol	15.17	17.30	18.90	21.60	23.00	21.60
3.	Methyl isobutyl ketone	17.00	20.55	23.10	24.50	27.20	26.20
4.	n-butyl acetate	20.58	24.91	26.50	29.13	30.80	30.26
5.	p(m)-xylene	25.54	27.72	30.30	32.12	32.40	32.62
6.	o-xylene	26.50	29.50	32.40	32.83	33.40	34.00

It is seen from the dependence of dissolution heat on the amount of liquid phase (Fig. 2.) that the heats of dissolution of the compounds in the liquid phase OV-101 applied on Chromosorb W AW DMCS are increased when the amount of liquid phase increases up to 10%. With further increase in the amount of liquid phase, the values of dissolution heat are kept at the same level. Hence, one can state when the amount of liquid phase OV-101 on the support is not less than 10%, then, it is the dissolution process which mainly takes place, and the adsorption phenomena at the interface of liquid – gas can reveal only a negligible effect on the separation of the compounds under investigation. It was found that a good separation of the investigated compounds in obtained when 10% OV-101 is deposited on Chromosorb W AW DMCS. With higher amount of liquid phase, the efficiency of chromatographic column decreases, which deteriorates the resolution power.

Other parameters of the column operation were also studied, i.e. column temperature, flow rate of carrier gas (argon). The
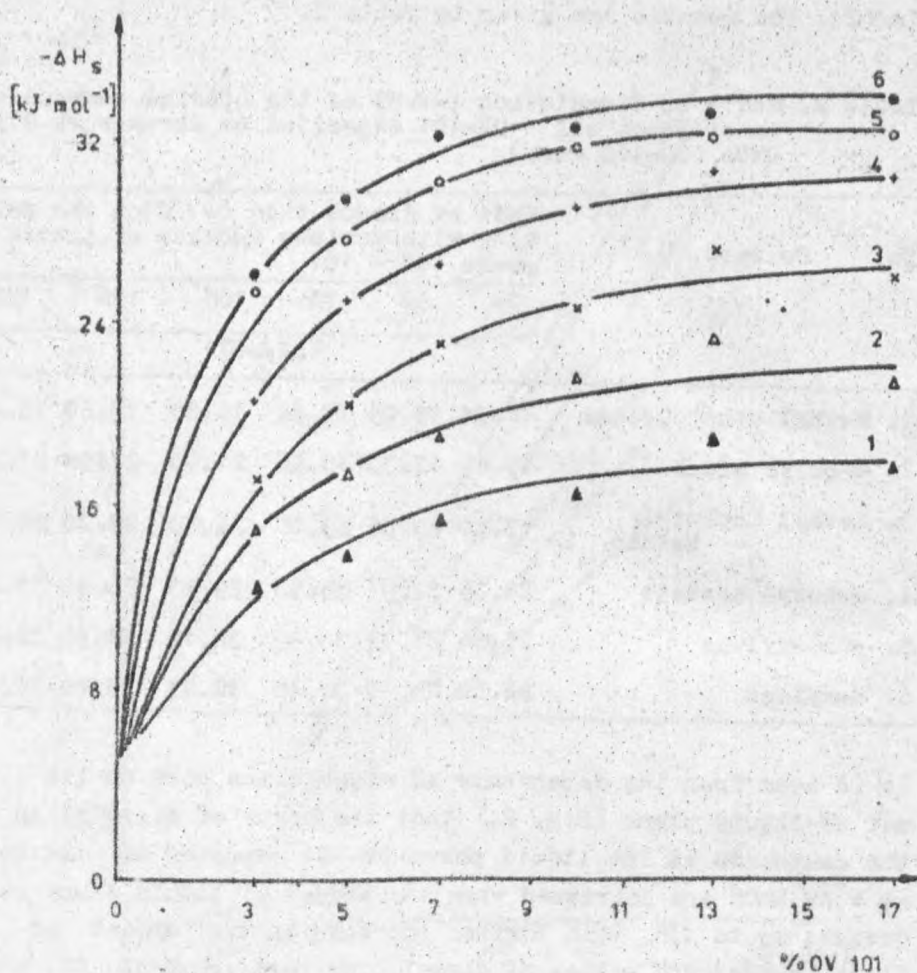
Fig.2. Relationship between heat of solution $(-\Delta H_S)$ and percentage of coating liquid phase OV-101 on Chromosorb W AW DMCS for the compounds as in Fig. 1.

best conditions for chromatographic separation were obtained when using a steel column 3 m in length and 4 mm in iner diameter, filled with liquid phase OV-101 applied in anamount of 10 % by wt. on Chromosorb W AW DMCS (80-100/mesh) at the following parameters of chromatographic operation:

- flow rate of argon - 30 cm^3/min

- flow rate of hydrogen - 30 cm^3/min
- flow rate of air - 300 cm^3/min
- initial column temperature - 353 K
- time of isothermic work - 12 min
- final column temperature - 403 K
- temperature increase rate - 298 K/min
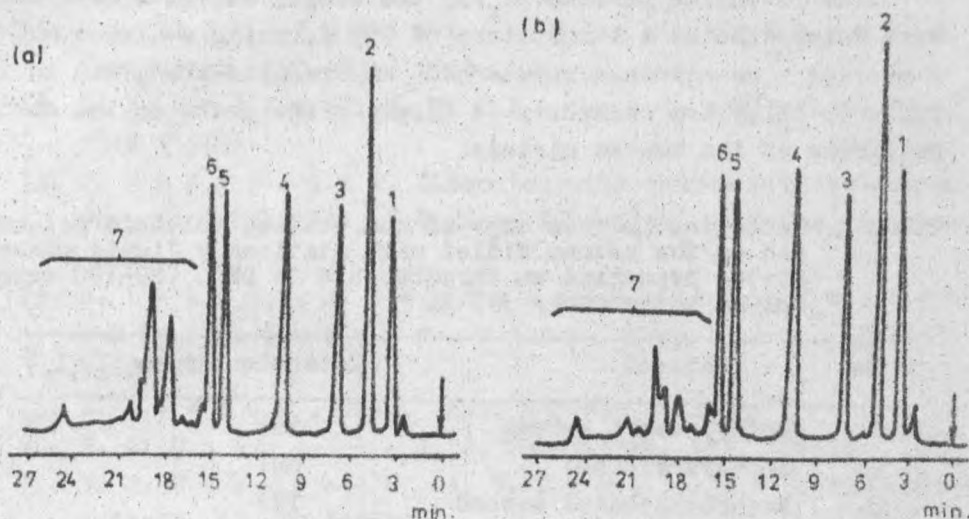- detector temperature 433 K
- sample injector temperature 503 K

Fig. 3. Chromatograms of the investigated mixtures of solvents:
a) batch I, b) batch II   Peaks: 1 - methyl ethyl keto-
ne; 2 - n-butyl alcohol; 3 - methyl isobutyl ketone;
4 - n-butyl acetate, 5 - p- m -xylene; 6 - o-xylene.

The obtained chromatographic separation of the mixture under
investigation is illustrated in Fig 3 (a and b). Chromatograms
a and b are different in this that the petroleum spirits and
solvent naphtha used in mixtures a and b are taken from differ-
ent sources. The presented chromatograms show that the compo-
sitions of petroleum spirits and solvent naphtha are variable
and depend on the tested batch of solvent, however, it does not
prevent from good separation of the remaining simple solvents
under the proposed conditions of analysis.

Also retention indices (I_x) of the simple solvents separated
were determined at a temperature of 353 K, using n-hexane and
n-heptane   as standard substances. The results are given in
Table 3. They are necessary to identify the peaks on the chro-
matograms of the tested mixture.

Table 3. Retention indices (I_x) of the studied solvents determi-
         ned on the column filled with stationary liquid phase
         OV-101 deposited on Chromosorb W AW DMCS (80-100 mesh).
         Column temperature 353 K.

No	Solvent	Retention index (I_x)
1.	Methyl ethyl ketone	583
2.	n-butyl alcohol	651
3.	Methyl isobutyl ketone	722
4.	n-butyl acetate	805
5.	p(m)-xylene	883
6.	o-xylene	910

REFERENCES

1. NIOSH Manual of Analytical Methods, Cincinnati, Ohio,(1977),
   Vol. 2, Methods No S 3, No S.66, No S 47.
2. NIOSH Manual of Analytical Methods, Cincinnati, Ohio,(1977),
   Vol. 3, Method No S 318
3. J. K r a j e w s k i, K. N o w i c k a , Med. Pracy, 31,
   305 (1980)
4. A. K r e t z s c h m a r , Z. G r o s s , Z. Analyt. Chem.,
   277, 375 (1975)

5. K. Yu. S h a p o s h n i k o w, Z. A. S e m e n o w a ,
   Referat Zh. Khim., 16, 196 D(1969),Abstr. No 166204

6. J. R o u s s e a u , Ochr. Pracy, 53, 115 (1967)

7. E.S.K. C h i a n , P.P.K. K u o , Environ, Sci. Technol.
   11, 282 (1977)

8. B. L e v a d i e, S. M. M a c A s k i l l , Analyt. Chem.,
   48, 76 (1976)

9. J. C. G i d d i n s , Anal. Chem. 35, 439 (1963)

10. P. U r o n e, J. F. P a r c h e r , Anal. Chem. 38,270,
    (1966)

11. K u n i s h i g e N a i t o, S h i n a u k e T a k e i, J.
    Chromatogr. 190, 21 (1980)

12. R. A. K e l l e r , S. H. S t e w a r t, Anal. Chem. 34,
    1834 (1962)

13. T. P a r y j c z a k, Chromatografia gazowa w badaniach ad-
    sorpcji i katalizy, Państwowe Wydawnictwa Naukowe, Warszawa
    (1975), p. 173

14. R. L e b o d a, A. W a k s m u n d z k i, J. S k u b i s z e-
    w s k a, Z. S u p r y n o w i c z , Chem. Anal. 23, 397
    (1978)

15. R. L e b o d a , Chem. Anal. 23, 935 (1978)

16. R. C. C a s t e l l e s, J. Chromatogr. 111, 1(1975)

17. V. M. N a b i v a c h , A. V. K i r i l e n k o, Chromato-
    graphia 13, 29 (1980)

18. T. P a r y j c z a k, S. C z e r c z a k, Chem. Anal. 29,
    845 (1981)

19. E. K a l a s z n i k o w a, A. W. K i s i e l e w , J. Chro-
    matogr. 152, 433 (1978).

Joanna Masłowska, Krystyna Nowicka

OPTYMALIZACJA WARUNKÓW CHROMATOGRAFICZNEGO ROZDZIELANIA
MIESZANINY ROZPUSZCZALNIKÓW W OPARCIU O TERMODYNAMICZNE
PUNKCJE ADSORPCJI I ROZPUSZCZANIA

Wykorzystując dane chromatograficzne wyznaczono ciepła
adsorpcji na Chromosorbie W AW DMCS, oraz ciepła rozpuszczania
w fazie silikonowej OV-101, sześciu rozpuszczalników: ketonu
metylo-etylowego, alkoholu n-butylowego, ketonu metyloizobuty-
lowego, octanu n-butylu, p-ksylenu i o-ksylenu. Przebadano
zmiany w wartościach ciepła rozpuszczania badanych związków w
zależności od procentowej zawartości stacjonarnej fazy OV-101
osadzonej na Chromo-sorbie W AW DMCS. Wykazano, że wartości
ciepeł rozpuszczania wzrastają wraz z   zawartością fazy OV-101
aż do 10 % wag.

W oparciu o uzyskane wyniki opracowano chromatograficzną
metodę rozdzielania mieszaniny złożonej z powyższych rozpusz-
czalników, współwystępującej z solwentnaftą i benzyną lakową C.