STRUCTURE INVESTIGATION BY EVAPORATION OF VOLATILE HYDROCARBONS FROM MIXTURES OF HIGH VAPOUR PRESSURE DIFFERENCES

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Introduction

The methods of thermal analysis have been and are being used mainly for analysis. It was found also useful, however, to study physicochemical effects such as evaporation of liquids, determination of fictive evaporation surface [1, 2], determination of the Conradson number and flash-point of oil derivatives. In the present work it is attempted to derive information from evaporation thermogravimetric data about the structure of the liquids the volatile substance is mixed with.

Experimental

Water, benzene, toluene, n-tridecane n-heptane and cyclohexane were selected as volatile substances; hydrocarbons exhibiting aromatic, alkyl-aromatic, paraffin and naphtene characteristics. As non-volatile components n-paraffin having an average molecular weight of 260 was used and also oil residue containing 44.6% paraffin, 45.7% naphtene, 7.7% aromatic residue having an average molecular weight of 550. Although the non-volatile compounds represent quite a series of hydrocarbons the temperature range of their evaporation lies much higher than that of the volatile compounds. From this respect the non-volatile compound can be considered as a single component having very high boiling temperature.

Derivative thermogravimetric measurements were performed with a Paulik—Paulik—Erdey MOM type derivatograph [3] with the modification that the conical Pt-crucible was replaced by a cylindrical one. Atmospheric nitrogen was made to flow through the device during measurement.

Results and Discussion

Evaporation of pure liquids

TG and DTG curves of the pure liquids were recorded at different heating rates. The activation energies calculated from the recorded curves are shown in Table 1. It is seen that by increasing rate of heating the apparent activation energy of evaporation increases for water but generally decreases for benzene, toluene, n-heptane and cyclohexane and n-tridecane.

Table 1

The effect of heating rate on the activation energy of evaporation of pure liquids vs, temperature [kcal/mole]

Water

Temperature, °C	Heating rate, °C/minute		
	1.5	2.0	6.0
40— 60	13.0	14.0	—
60— 70	10.0	10.1	21.4
70— 80	9.3	9.6	17.3
80— 90	9.0	9.1	15.5
90—100	8.8	9.0	13.2
100—110	8.8	8.9	—
100—120	—	—	11.0

Other substances

Heating rate 3 °C/minute

Benzene		Toluene		n-Heptane		Cyclohexane	
T, °C	E, kcal/mole	T, °C	E, kcal/mole	T, °C	E, kcal/mole	T, °C	E, kcal/mole
25—65	10.5	25— 50	11.4	25— 45	9.5	25—65	10.8
65—80	14.4	50— 95	11.7	45— 90	10.3	65—80	13.7
80—87	20.2	95—113	16.0	90—100	15.6	65—90	28.3
87—88	31.4	113—117	45.0	100—106	27.8		

Heating rate 10 °C/minute

Benzene		Toluene		n-Heptane		Cyclohexane	
25—40	7.8	25— 80	8.5	25— 55	7.4	25—65	8.7
40—65	10.5	80—108	14.7	55— 70	10.3	65—95	16.5
65—77	17.8	108—115	33.0				

Table 2 shows a comparison between the measured and calculated rates of evaporation of water. Calculations were made assuming Boltzmann velocity distribution of an ideal gas using the following equation:

$$\frac{dn}{dt} = \frac{p_g}{\sqrt{2\pi\,MRT}} \tag{1}$$

where n is the mole number of the vapour condensed, p_g is the pressure, t is the time T is the temperature, M is the molecular weight, R is the gas constant.

Due to the independence of evaporation from condensation the rate of evaporation must be the same even if there is not condensation from the vapour phase.

The difference of four orders of magnitude between the measured and calculated values shown in Table 2 indicates that the practically effective evaporation surface is only a very small fraction of the geometrical one. It was shown earlier [1] that the effective evaporation surface depended not only on the gaseous phase but on the structure of the liquid as well.

Table 2

Calculated and measured rates of evaporation
of distilled water; 6 °C/minute

Temperature, °C	Evaporation rate [mg/(cm²s)]	
	theoretical	measured
50	1.15×10^3	1.10×10^{-2}
80	4.22×10^3	1.33×10^{-1}
93	6.94×10^3	3.20×10^{-1}
100	8.84×10^3	4.75×10^{-1}
108	10.30×10^3	6.00×10^{-1}
117	15.65×10^3	8.90×10^{-1}
125	20.90×10^3	1.19

It can be ascertained from Fig. 1 showing the logarithm of the fictive evaporation surface (F'), determined as the quotient of the measured evaporation rate by the theoretical evaporation rate calculated from Eq. 1, versus the temperature reduced to the boiling point that the kinetics of evaporation of the examined hydrocarbons are very similar to each other but greatly differ from that of the water.

Kinetic equations

For calculation of rate constants and activation energies of evaporation, the following kinetic equation was used [1]:

$$\frac{dx}{dt} = A \exp. \left(-\frac{E}{RT}\right) \left(a - x\right)^n \tag{2}$$

Where dx/dt is the rate of evaporation, $[mg/(cm^2.s)]$; A is the preexponential factor, $[mg/(cm^2.s)]$; E is the activation energy [kcal/mole]; R is the gas constant [kcal/mole.K]; T is the temperature, [°K]; $(a - x)$ is the weight of the volatile component present in the sample holder at temperature T, [mg]; n is the kinetic order of the process.
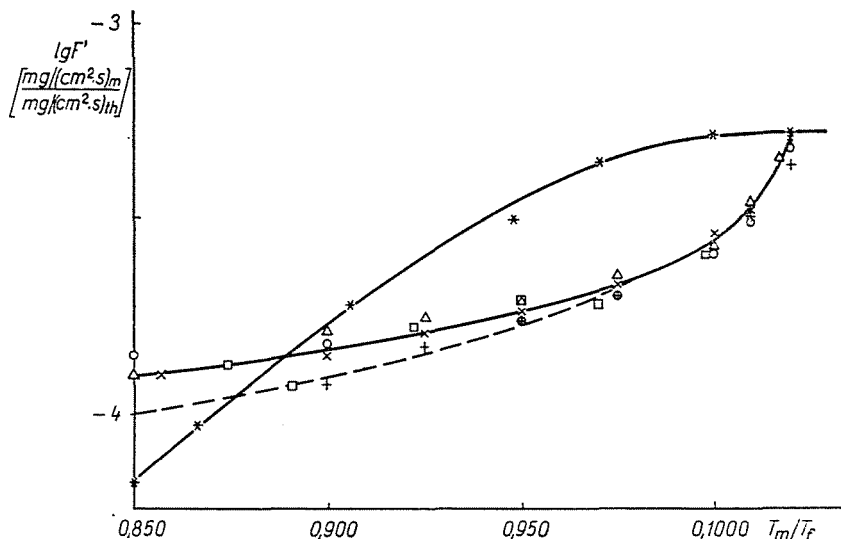

Fig. 1. Logarithm of fictive evaporation surface of pure liquids vs. temperature reduced to the boiling point. Heating rate 3 °C/minute. ✕ = Water; × = benzene; △ = toluene; + = cyclohexane; o = n-heptane; △ = n-tridecane; m = measured; th = theoretical; f = boiling point

In the case of evaporation of pure liquids the process-order is zero, accordingly:

$$\frac{dx}{dt} = A \exp \left(-\frac{E}{RT}\right) \tag{3}$$

Effect of the non-volatile component on evaporation

Samples amounting to 500 mg containing 50% of non-volatile components were measured at heating rates of 3 and 10°C/minute. From the recorded TG and DTG curves according to Eq. 2 the kinetic order of the process (n) and the activation energy were determined. The results are shown in Table 3. The n-values and the apparent activation energies are seen to be affected by the heating rate and by the kind of the non-volatile compound, too.

Table 3

Effect of presence of non-volatile component on the evaporation kinetics

Volatile component	Non-volatile component	Heating rate, °C/minute	ΔT Temperature range, °C	T_p Temperature at DTG peak, °C	n Kinetic order	E Activation energy, kcal/mole
Benzene	residual oil	3	20—140	89	1.0	10.8
	residual oil	10	30—175	98	1.0	12.8
	n-paraffine	3	30—175	103	1.0	9.05
	n-paraffine	10	35—190	105	1.0	11.4
Toluene	residual oil	3	35—175	114	1.0	9.6
	residual oil	10	40—220	130	1.5	11.9
	n-paraffine	3	30—185	122	1.0	10.9
	n-paraffine	10	40—210	136	1.5	11.5
Cyclohexane	residual oil	3	30—150	85	1.0	9.85
	residual oil	10	30—215	100	1.5	12.3
	n-paraffine	3	30—160	96	1.0	8.6
	n-paraffine	10	35—190	110	1.5	12.0
n-Heptane	residual oil	3	30—190	93	1.0	11.4
	residual oil	10	35—180	104	1.0	14.6
	n-paraffine	3	35—170	101	1.0	9.4
	n-paraffine	10	40—200	130	1.0	10.0

The effect of the presence of the non-volatile compound is illustrated in Figs 2 and 3 where the temperature dependence of the evaporation rates of the pure volatile compounds is compared with that of the mixtures. At low temperatures the volatile component is seen to evaporate from the mixture at a higher rate than from the pure state. As the effective surface of the mixture is obviously smaller than that of the pure liquid, it is concluded that the non-volatile liquid acts as an accelerator to the evaporation process as if the volatile component would be squeezed out of the non-volatile matrix. This shows the importance of the structure of the liquid for the evaporation process.

More marked is the dependence of the non-volatile component on the evaporation kinetics of the volatile one at low volatile component con-centrations. Table 4 shows the temperature intervals (ΔT), the peak-temperatures (T_p), the orders of the process (n) and the apparent activation energies (E) of the mixtures at different concentrations. For decreasing con-centration of the volatile component the activation energy is seen to decrease the DTG peak-temperature to slightly increase and the temperature range of the process to extend, especially because the high temperature limit is shifted
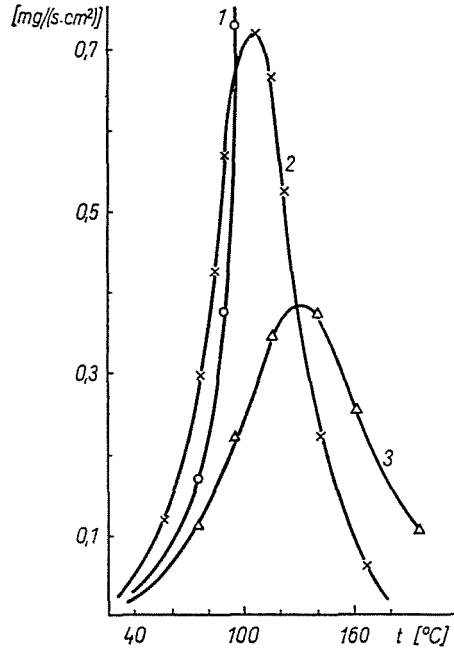
Fig. 2. The evaporation rate of n-heptane. 1. For pure n-heptane; 2. mixed with about 50% of residual oil; 3. mixed with about 50% of n-paraffin
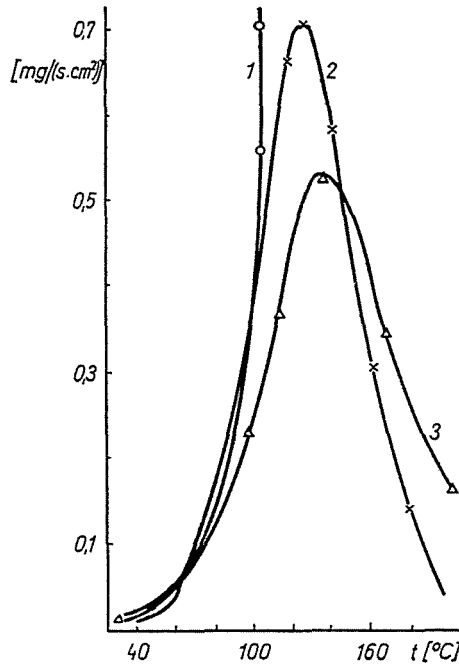

Fig. 3. The evaporation rate of toluene. 1. For pure toluene; 2. mixed with about 50% of residual oil; 3. mixed with about 50% of n-paraffin

Table 4

The dependence of the evaporation kinetics on the concentration
of the non-volatile component in oil residue mixtures

Volatile component	Concentration, %	ΔT Temperature range, °C	T_p Temperature at DTG peak, °C	n Kinetic order	E Activation energy, kcal/mole
Benzene	18.5	30—260	127	1.0	7.3
	57.0	35—200	110	1.0	12.8
	69.0	35—180	100	1.0	13.6
Toluene	24.0	40—245	132	1.5	9.4
	51.0	40—220	130	1.5	11.9
	67.0	40—220	132	1.0	12.4
Cyclohexane	25.0	30—280	100 (160)	x	x
	48.0	30—215	100	1.5	12.3
	59.0	30—210	99	1.0	14.2
n-Heptane	19.0	30—190	128	1.0	10.9
	61.0	35—180	104	1.0	13.5
	75.0	30—190	104	1.5	17.0

x = not determined
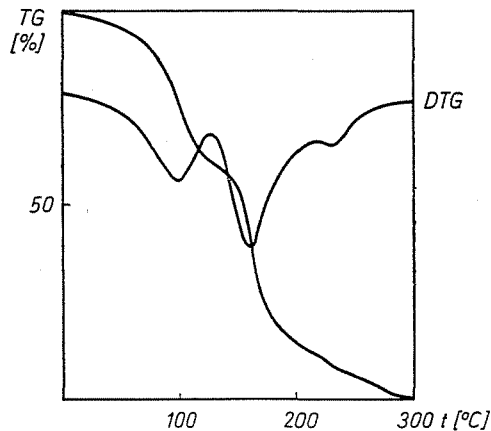
Fig. 4. TG and DTG curves of the mixture of 25% cyclohexane and 75% residual oil

up. At low concentrations the TG and DTG curves exhibit a certain structure
as it is shown in Fig. 4 for 25% of cyclohexane in oil residue.

For the sake of comparison, in Fig. 5 the corresponding 59% cyclo-
hexane mixture is shown. The DTG curve of the 25% mixture is seen to exhibit

such a character as if different compounds were successively evaporated. A similar effect was found in 7% of benzene to residual oil mixture (Fig. 6) while at 69% benzene concentration (Fig. 7) a usual single-peak curve was obtained.

The observed effect of the non-volatile additive on the evaporation kinetics is tentatively explained by assuming that the molecules of the non-volatile component are resolved by the volatile molecules at high concentrations preventing structure formation. At low concentrations this solution becomes incomplete, a structure of the non-volatile compound is formed through which the volatile molecules must diffuse on to the surface to evaporate. This liquid structure is reflected by the multiplicity of the DTG peaks shown in Figs 4, 6 and by different curves in Fig. 8 which show the fictive
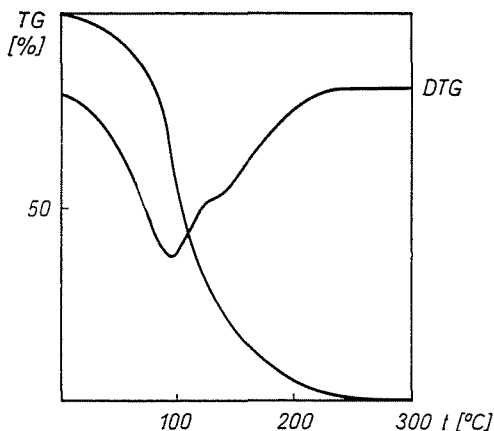
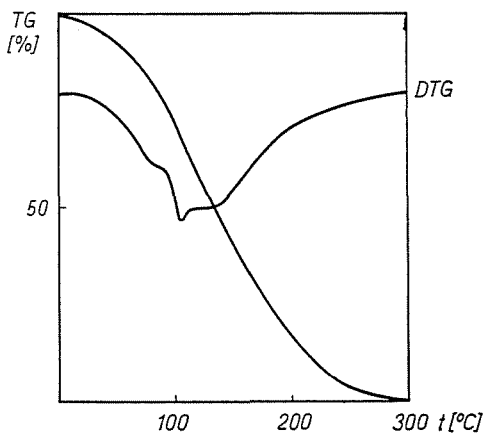Fig. 5. TG and DTG curves of the mixture of 59% cyclohexane and 41% residual oil

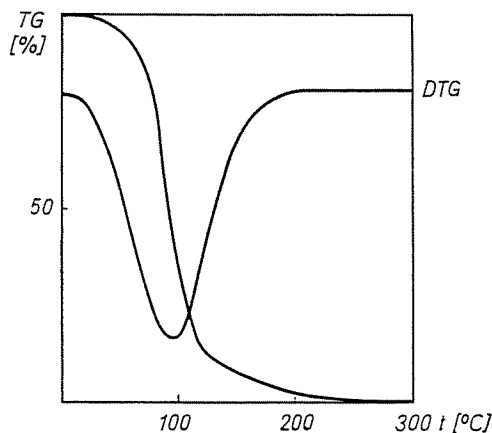Fig. 6. TG and DTG curves of the mixture of 7% benzene and 93% residual oil

Fig. 7. TG and DTG curves of the mixture of 69% benzene and 31% residual oil
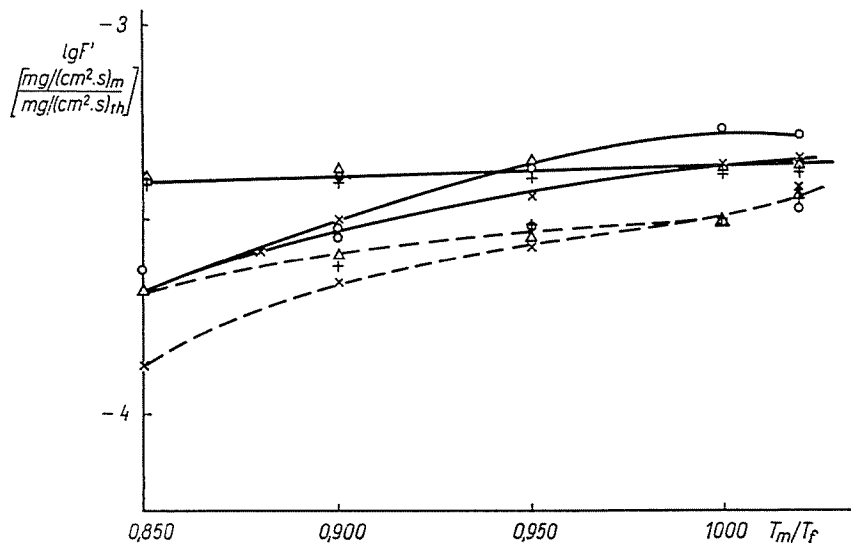

Fig. 8. Logarithm of fictive evaporation surface of different hydrocarbons evaporating out of the non-volatile matrix vs. temperature reduced to the boiling point. $\times$ = Benzene; $\triangle$ = toluene; $+$ = cyclohexane; o = n-heptane; ———— residual oil; heating rate 3° C/minute; ----- n-paraffin, heating rate 10 °C/minute

evaporation surface of the volatile component of different mixtures versus the temperature reduced to the boiling point.

According to this picture the diffusion constant of the volatile compound in the non-volatile matrix should be important in determining evaporation kinetics. The diffusion constant has been estimated by the equation of WILKE and CHANG [4]:

$$D_1 = 7.4 \cdot 10^{-8} \frac{(_aM_2)^{0.5}T}{\eta_2 V_1^{0.6}} \tag{4}$$

where D_1 is the diffusion constant, $[cm^2/s]]$; T is the temperature, $[K]$; a is an association factor, of unit value for non associated liquids; M_2 is the molecular weight of the solvent; η_2 is the viscosity of solvent $[cp]$; V_1 is the molar volume of the dissolved material, $[cm^3/mole]$.

Figs 9 and 10 show the calculated temperature dependence of the diffusion constants of the volatile compounds in pure n-paraffin and in oil residue, respectively. Despite the probable errors in determination of the temperature dependence of viscosity and of the association factor, a significant difference between the temperature dependence of the diffusion constants of these two non-volatile components was found.
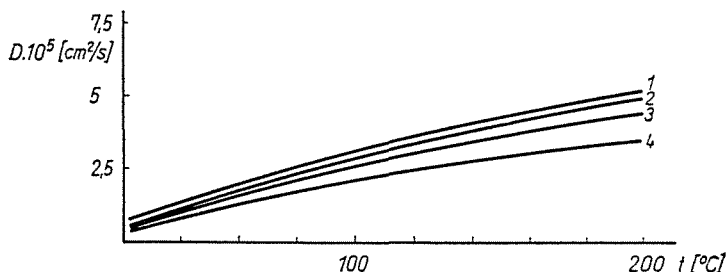

Fig. 9. Temperature dependence of the diffusion constants of benzene (1), toluene (2), cyclohexane (3) and n-heptane (4) in n-paraffin
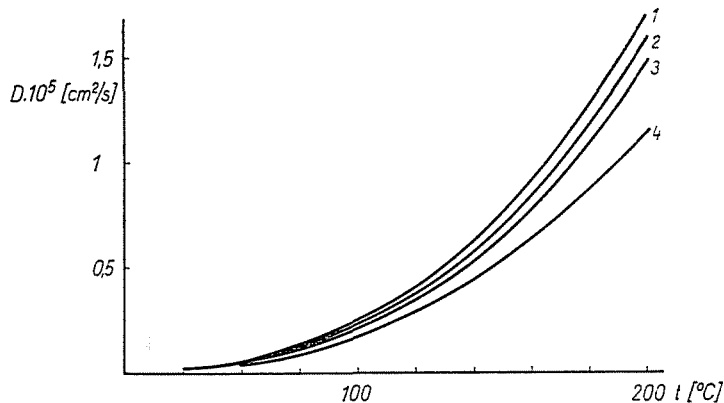

Fig. 10. Temperature dependence of the diffusion constants of benzene (1), toluene (2) cyclohexane (3) and n-heptane (4) in oil residue

Conclusions

From the observed dependence of the evaporation kinetics on the presence of non-evaporating components it is concluded that the process of evaporation includes two main stages, one is the diffusion on to the surface, the other is

evaporation. Thus, by using small concentrations of low boiling temperature matrix it becomes possible to derive information about the structure of the liquid matrix from the TG and DTG curves of evaporation.

Acknowledgements

Summary

Evaporation kinetics of water, benzene, toluene, n-heptane and cyclohexane were studied by the derivative thermogravimetric method in the presence of non-volatile components such as n-paraffins and oil residue.

The rates of evaporation of the pure liquids were found to be superior by four orders of magnitude than the calculated ones assuming Boltzmann equilibrium.

Additives having high vapour pressures were found to appreciably affect the evaporation kinetics. This is especially marked at low concentrations of the volatile component. In such cases DTG curves for evaporation rate versus temperature exhibit multiple peaks rather than a single one. This effect is attributed to the structure of the non-volatile liquid through which to volatile one should diffuse before evaporation.

References

1. ADONYI, Z.: Thermal Analysis. Proc. 3rd ICTA Davos Switzerland. Basel—Stuttgart, Vol. 1. p. 255. (1972)
2. ADONYI, Z.: Periodica Polytechnica Chem. Eng. 16, 285 (1972)
3. PAULIK, F.—PAULIK, J.—ERDEY, L.: Fresenius' Anal. Chem. 160, 241 (1958)
4. WILKE, C. R.—CHANG, P.: A. J. Ch. E. Journal 1, 264 (1955)

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