A UNIQUE OSCILLATORY PHENOMENON REVEALED BY A MICROWEIGHING METHOD

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Abstract

An earlier study of the interaction between solid urea and *n*-octane vapour in the presence of non-complex-forming hydrocarbons by means of a vacuum microbalance technique revealed the oscillatory nature of urea–octane inclusion compound (complex) formation: process damping, occurrence in the reverse direction and repeated renewal without attainment of the complete saturation of the urea with octane.

The phenomenon is interpreted on the basis of the recently discovered oscillatory adsorption, regarded as the surface competition between the spottily adsorbed A and B components, which results alternatively in spontaneous transitions from a state 'A in B' to a state 'B in A' and *vice versa*, with simultaneous dramatic change in the spot configurations under A and B, as well as changes in the chemical potentials of adsorbed A and B at the inversion points, certain minimal parts of the surface under A and B being permanently occupied by each of the components. This latter signifies that the non-complex-forming hydrocarbon hinders the complete transition of the urea to its inclusion compound phase.

Keywords: oscillatory urea–octane complex formation, quantitative evaluation of area under adsorption spots, spotty competitive oscillatory adsorption, vacuum microweighing technique

Introduction

In 1968, when the first part [1] of the present work was published, it was known that, on contact with liquid normal paraffins, dissolved or solid urea crystallizes or recrystallizes in such a way that each paraffin molecule is included in a cavity in the hexagonal lattice of the urea, as contrasted with the usual tetragonal urea lattice (Fig. 1). Such compounds have been called urea inclusion compounds, urea molecular complexes, or simply urea complexes (these expressions may be used as synonyms). Very little information was available at that time concerning the interaction between tetragonal urea and *n*-paraffin vapour. The only published investigation was that of McAdie and Frost [2], in which the microweighing method was first applied for this purpose.

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$$Urea_{dissolved} + n\text{-paraffin}_{liquid} \Leftrightarrow urea\text{-paraffin complex}_{hexagonal}$$

$$Urea_{tetragonal} + n\text{-paraffin}_{liquid} \Leftrightarrow urea\text{-paraffin complex}_{hexagonal}$$
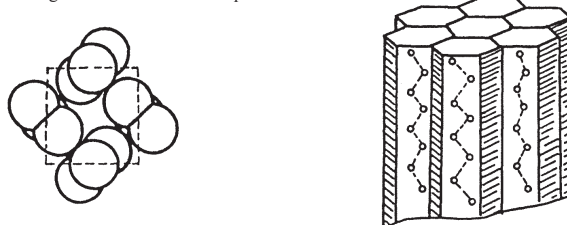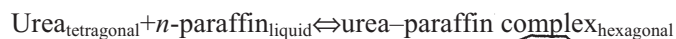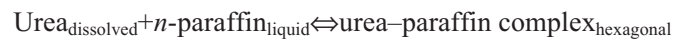

Fig. 1 Complex formation between urea and *n*-paraffins

The idea of microweighing was adopted, but in contrast with McAdie and Frost, [2], who used pure *n*-octane vapour, in our work binary vapour mixtures of octane with non-complex-forming hydrocarbons (benzene, cyclohexane, and *n*-propylbenzene) were used [1].

The present work aims to utilize current conceptions to interpret a unique phenomenon reported in 1968, but which was completely incomprehensible to us at that time.

Experimental

Figure 2 outlines the set-up used [1] to study the complex formation. The liquid mixture (1) of *n*-octane and non-complex-forming hydrocarbon (molar ratio=0.715:0.285 in all
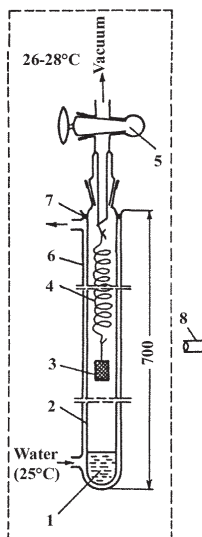

Fig. 2 Set-up for study of complex formation; 1 – binary liquid mixture of *n*-octane with non-complex-forming hydrocarbon; 2 – tube; 3 – basket with urea; 4 – quartz spiral; 5 – stopcock; 6 – water jacket; 7 – rubber ring; 8 – cathetometer

cases) was placed into the tube (2) via a pipette. About 300 mg of solid urea, previously activated in acetone [3], was weighed into a small gauze basket (3) and suspended from a quartz spiral microbalance (4) with sensitivities of 3.425 and 5.301 mg (for two different spirals) per mm extension. With the stopcock (5) closed, the mixture was frozen by means of liquid nitrogen. When the stopcock (5) was open, the tube (1) was connected with vacuum. After evacuation at room temperature for 2 h, the stopcock (5) was closed, and the tube (1) was placed into the empty water jacket (6) and fastened there by a suitable rubber ring (7). The length of the spiral was measured to ±0.01 mm accuracy with a rigidly mounted cathetometer (8). The pump circulating the thermostat water (water temperature 25°C) was started, and zero time for the reaction was taken as this point. This was generally 2–3 min after the tube (1) containing the frozen mixture was placed into the water jacket (6). The set-up described was enclosed in a thermostatically controlled (26–28°C) cabinet. The reaction proceeded to constant mass. The partial pressure of octane was in all experiments 10 mm Hg, whereas the partial pressure of each of the other hydrocarbons was determined by its saturated pressure at 25°C and by its given molar fraction in the liquid mixtures.
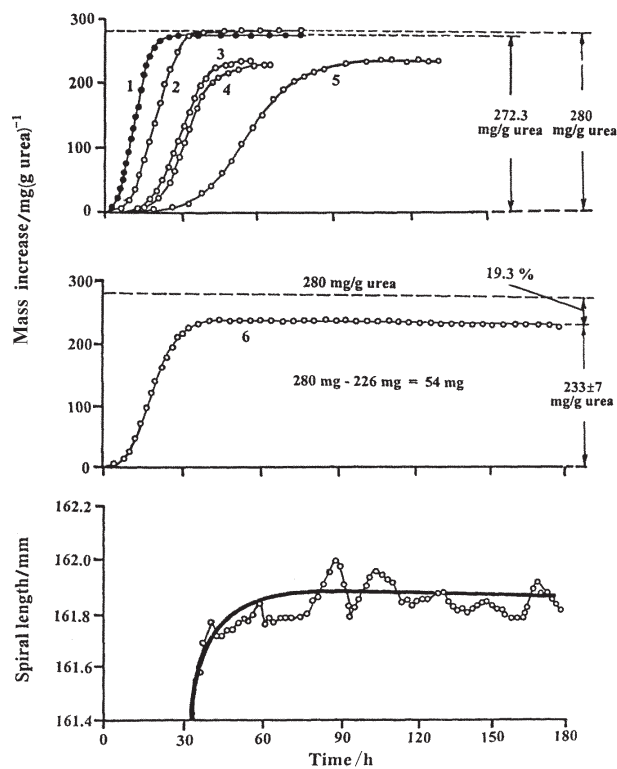

Fig. 3 Kinetic curves of complex formation; 1, 2 – customary kinetic curves (1 [2], 2 [1]); 3–6 – anomalous kinetic curves [1] with an enlargement of the final part of curve 6 (at the bottom)

The complex formation was completed as a rule in 30–40 h, though some experiments lasted nearly 200 h.

The kinetic curves for this process had the usual goose-neck appearance [2].

In consequence of complex formation, urea includes up to 28 mass% of octane and the spiral tension is therefore considerable (10–20 mm for the given sensitivities and mass of urea), which ensures a measurement accuracy of ±0.01%.

Despite the non-stoichiometry of the urea complexes, they are formed in constant composition. However, the complex compositions determined by different methods differ slightly, as can be seen from Table 1 for the urea–octane complex data.

The last two compositions (mass ratio equivalents 272.3 and 280±1), obtained by the same precise technique (Table 1), will be taken into further consideration. The formation of the compounds with these two compositions is illustrated by curves 1 and 2 in Fig. 3 [1, 2, 8]. It is of interest that for such compositions the experimental points lie on the corresponding lines with mathematical regularity.

Table 1 Compositions of urea–octane complex determined by different methods

Method	Urea/octane molar ratio	Mass ratio equivalent/ mg octane/g urea	Reference
Chemical analysis	7.0	271.4	[4]
Chemical analysis	7.18	264.6	[4]
Physicochemical (wet residue, concentration change)	6.73	282.2	[5]
Physicochemical (three-phase diagram analysis)	7.0	271.4	[6]
X-ray analysis	6.97	272.7	[7]
Microweighing	6.98	272.3	[2]
Microweighing	6.8	280±1	[1]

Quite another picture is reflected by curves 3–6. First of all, the essentially lower amount of octane included by urea is striking: only 233±7 mg. The maximum difference relative to 280 mg is 54 mg or 19.3%. More interesting is the fact that the experimental points no longer lie on the lines with the previous mathematical regularity. Still more curious is the pulsing reverse occurrence of the process within the horizontal parts of the function, which is especially interesting at their endings: the impression emerges that the complex formation is still not completed, but it cannot be completed because any progress here is smoothed at once by the reverse process. It appears as if the system is striving to surmount an invisible barrier, but is not able to do this when it reaches the horizontal parts of the function. The final part of curve 6 is depicted on an enlarged scale at the bottom of Fig. 3. The horizontal part of the line corresponds on average to 233 mg octane. The line thickness denotes the exactness of the measurement. It can be seen that the oscillations in the mass exceed the exactness of the measurement by one order or even more.

In 1965, when the described investigations were first performed, it was not possible to attain the required reproducibility of the presented experimental results; in

the overwhelming majority of the cases, the compounds with the normal composition were formed, without any anomalies. Unfortunately, we did not return to this subject, mainly since a meaningful interpretation of the results obtained was not foreseeable.

The maximum duration of an experiment was 178 h, with the development of more or less stationary oscillations. The possible continuation of such oscillations remains an open question: would they be virtually endless, or would they gradually stop? An experimental search for the answer is probably hopeless, and it is obvious, therefore, that a search should be made theoretically.

Discussion

Not too long ago, the phenomenon of the oscillatory adsorption of two components A and B revealed [9, 10]. It has been hypothesized [11] that the phenomenon is caused by a number of factors, such as the competitive coverage of the surface by components A and B, the 'spotty' nature of component adsorption, the dramatic change in the configuration of such 'spots' at a certain step during surface coverage by one of the components, resulting in a transition of the adsorption layer from an 'A in B' state to a 'B in A' state and *vice versa*, and the dependence of the values of the chemical potentials of A and B on the configuration of the adsorption 'spot', causing a change in the direction of the sorption process.

An attempt has been made [12] to examine the phenomenon from the aspect of non-equilibrium thermodynamics. By relying on the Gibbs equation, particularly with respect to the flux and affinity equations, and taking into account the equality of the reciprocal influence coefficients, it is possible to conclude that the chemical potentials of the competitive components at the periphery of the sorption 'spots' are either equal or approximately equal. This indicates that the entropy of the system remains constant (i.e. $dS=0$), leading to the possibility of sustained oscillations occurring in the adsorption process.

If one proceeds from the above simple model of the alternative coverage of the surface by one and then the other component, it would be quite evident that the spot areas under each of them are 'breathing' within the certain minimum and maximum values. These values for the given model are 21.5 and 78.5% of the total adsorbent area [12]. That is, below 21.5% of its value, the area cannot be 'stripped' of either component; in other words 21.5% of the area remains permanently 'blocked' by each of the components. It is of interest that the maximum values found experimentally for the competitive systems 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl-octane and 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl-benzene proved to be practically equal, 74.5 and 75.4%, respectively [10], which gives the minimum values as 24.6 and 25.5%, respectively, exceeding the calculated minimum value by a relative amount of 15–20%.

Naturally, complex formation also proceeds as a heterogeneous 'solid–vapour' process through the adsorption of the complex-forming and non-complex-forming components on the urea surface. Both components may certainly give rise to competitive oscillatory adsorption. It is clear that the complex-forming component cannot occupy the total urea surface: some minimum part of it will remain under the 'spots'

of the non-complex-forming component. In this case, certain phenomena should be observe:

- irregularity of complex formation through intervention of competitive adsorption in the course of the process;
- incompletion of complex formation;
- in and out process in the horizontal parts.

All these are in fact observed. As regards the incompletion of complex formation to the above-mentioned extent of 19.3%, the given value is less than the minimum value of the permanently 'blocked' surface area considered above 21.5% by a relative amount of nearly 10% as compared with 15–20% for oscillatory adsorption.

This seems to be another demonstration of the correctness of the oscillatory adsorption model and of oscillatory adsorption being the reason for the oscillatory occurrence of urea–octane complex formation in the presence of non-complex-forming components.

Conclusions

The use of the microweighing technique for the study of systems which appear to be practically exclusively investigated by the usual method of the immediate agitation of massive solid or dissolved urea phases with massive liquid hydrocarbon mixtures has led to the important observation of an unknown oscillatory process, which is now interpreted from the standpoint of the recently revealed phenomenon of the competitive oscillatory adsorption of two components.

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