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Abstract

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DETERMINATION OF THE THERMODYNAMIC CONSTANTS OF MOLECULAR COMPOUNDS BY THE METHOD OF DIELECTROMETRIC TITRATION

(Presented by Academician S. S. Medvedev, 12 XII 1963)

To characterize intermolecular interaction and the properties of molecular compounds, it is very important to know the thermodynamic parameters of the corresponding reactions.

In the present study a new method has been developed for determining equilibrium constants, heat effects, and also changes in free energy and entropy during complex formation in solutions.

The method of dielectric polarization has been taken as the basis, in the variant of the previously developed method of dielectrometric titration (^1). The essence of this method consists in measuring changes in the dielectric constant ε and density d of solutions of component A in a nonpolar solvent upon the successive addition of small portions of component B. If a complex AB with a dipole moment different from the dipole moment of the added component B is formed in the system, then the dielectrometric titration curve for systems of the type

$A + B \rightleftarrows AB$

usually has the form mnl (Fig. 1).

Fig. 1. General form of dielectrometric titration curves for systems of the type $A + B \rightleftarrows AB$

By extrapolating the initial segment of the ε—C and d—C curves, the dipole moment of compound AB is determined under conditions of suppressed dissociation. By extrapolating the second (after the bend) segment of the curves, the dipole moment of the added component B is determined.

The deviation of the experimental curve mnl from the extrapolated curve mkl is caused by dissociation of the complex into components. The magnitude of this deviation kn characterizes the instability of the molecular compound.

Using the rule of additivity, the specific polarization of the solution at point n can be expressed as follows:

$$p = p_A(W_A - \Delta W_A) + p_B(W_B - \Delta W_B) + p_{AB}(\Delta W_A + \Delta W_B) + p_p W_p, \quad (1)$$

where p_A, p_B, p_{AB}, and p_p are the specific polarizations of components A and B, the complex, and the solvent, respectively; W_A, W_B, W_p are the weight fractions of the components and solvent in the system; ΔW_A and ΔW_B are the weight fractions of the components that have entered into the complex. The quantities p and p_{AB} are determined from the corresponding values of ε and d at points n and k. The polarization values of the components and solvent (p_A, p_B, and p_p), at their concentrations corresponding to point n, are determined experimentally.

From equation (1), using the relation $\Delta W_A/\Delta W_B = M_A/M_B$, where M_A and M_B are the molecular weights, one can determine the weight fractions of components A and B (ΔW_A and ΔW_B) that have entered into the complex.

The equilibrium constant of the complex-formation reaction

$$K = \frac{[\mathrm{AB}]}{[\mathrm{A}][\mathrm{B}]}$$

can be calculated by the formula:

$$K = \frac{(\Delta W_A + \Delta W_B) \cdot M_A \cdot M_B}{(W_A - \Delta W_A)(W_B - \Delta W_B)(M_A + M_B) \cdot d \cdot 1000} \text{ l/g-mol.} \quad (2)$$

To determine the heat of formation of the complex from the components and other thermodynamic constants, curves of dielectrometric titration are recorded at different temperatures.

Table 1

Equilibrium constants of complex-formation reactions
$\mathrm{R_2S + J_2 \rightleftarrows R_2S \cdot J_2}$

Sulfide in the sulfide–iodine system	T, °C	K, l/g-mol
Dibutyl sulfide	10	763
Dibutyl sulfide	25	365; 403
Dibutyl sulfide	40	219
Diamyl sulfide	10	641
Diamyl sulfide	25	383; 341
Diamyl sulfide	40	209
Dioctyl sulfide	25	746

Sulfide in the sulfide–iodine system	T, °C	K, l/g-mol
Dioctyl sulfide	40	423
Dioctyl sulfide	50	283
Thiophane *	10	1890
Thiophane *	25	833
Thiophane *	40	408
Dibenzyl sulfide	25	614
Dibenzyl sulfide	40	401
Dibenzyl sulfide	50	375

* The experiments were carried out in benzene because of the limited solubility of the complex in octane.

Table 2

Thermodynamic constants for the systems
$R_2S + J_2 \rightleftarrows R_2S \cdot J_2$

<table>
<tr><th>Sulfide</th><th>$-\Delta H$, kcal/g-mol</th><th>$-\Delta F_{298}$, kcal/g-mol</th><th>$-\Delta \bar{S}$, cal/deg · g-mol</th></tr>
<tr><td>Dibutyl sulfide</td><td colspan="3">7.6$±0.4|3.55±0.03|13.6±0.9||Diamylsulfide|7.0±0.3|3.51±0.03|11.7±0.9||Dioctylsulfide|7.4
|7.8–8.3|3.08–3.14|15.9–17.6||Thiophane|8.8±0.1|4.02±0.03|16.0±0.4||Thiophane*
|7.8–8.7|3.30–3.10|15.0–18.7||Dibenzylsulfide|4.8±0.3|3.83±0.03|3.26±$1.0</td></tr>
</table>

* Determined by spectroscopy ([8,9]).

It should be noted that the method of dielectric polarization in its usual form has been used in a number of works ([2–5]) to determine the dissociation constants of molecular compounds. However, owing to the cumbersomeness and complexity of the experiment, the question of other thermodynamic parameters was not considered in these works.

The method of dielectrometric titration makes it possible, comparatively simply, to measure equilibrium constants at different temperatures and to determine the heat effects ΔH, the changes in free energy ΔF, and entropy ΔS in the process of complex formation.

For evaluating the strength of molecular compounds it is very important to know the values of ΔH, ΔS, and ΔF. Estimating the stability of complexes only on the basis of dissociation constants can lead to errors, since it is necessary to take into account the change in entropy during reactions.

As examples of systems of the type $A + B \rightleftarrows AB$, in the present work the processes of formation of complexes of organic sulfides with iodine in octane were studied. The list of systems and the values of the equilibrium constants K at different temperatures are given in Table 1.

The concentrations of the solutions in different experiments were 0.02-0.06 g-mol/l. The accuracy of determining K is 5-6%.

Figure 2 gives the experimental results in the coordinates $\lg K$—$1/T$. As can be seen, the dependence $\lg K$—$1/T$ for all systems in the investigated temperature range is linear in character, and the points fit well on straight lines. From the temperature dependence of the con-

equilibrium constants, in accordance with the equation $\ln K = -\Delta H/RT + \Delta S/R$, ΔH and ΔS were determined.

Next, changes in free energy ΔF_{298} were calculated. The data obtained are given in Table 2, where the values of the thermodynamic quantities for the diethyl sulfide—iodine (No. 4) and thiophane—iodine (No. 6) systems, found by the spectroscopic method, are also indicated ($^{6-9}$).

It was of interest to compare the results obtained by the method of dielectrometric titration (d.k.t.) with the data of direct calorimetric measurements.

The thermal effects and equilibrium constants of the reactions of iodine with dibutyl sulfide and with thiophane were determined by means of the calorimetric titration (k.t.) method developed in our laboratory. The results are given in Table 3.

Fig. 2. Temperature dependence of the equilibrium constant for iodine—sulfide systems: 1 —diamyl sulfide, 2 —dibutyl sulfide, 3 —thiophane, 4 —dioctyl sulfide, 5 —dibenzyl sulfide.

Table 3

System	$-\Delta H$, kcal/g-mol, d.k.t. method	$-\Delta H$, kcal/g-mol, k.t. method	K, l/g-mol ($t = 25$°C), d.k.t. method	K, l/g-mol ($t = 25$°C), k.t. method
Dibutyl sulfide — iodine	7.6	8.2	365; 403	385
Thiophane —iodine	8.8	8.6	833	788

As is seen (Tables 2, 3), there is good agreement between the thermodynamic quantities obtained by different experimental methods. This fact is a criterion of the correctness of the proposed method for treating dielectrometric titration data.

The method of dielectrometric titration is thus very effective for the investigation of molecular compounds. On the one hand, as was established earlier (^{1}), it makes it possible to determine the composition of the compounds formed and their dipole moments under conditions of suppression of dissociation and, on the basis of these data, to judge the polarity of the intermolecular bond. On the other hand, as shown in the present work, with the aid of this method it is possible to measure the thermodynamic parameters of complex-formation reactions and thereby to obtain information on the strength of the intermolecular bond.

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