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Abstract

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SPECTROPHOTOMETRIC DETERMINATION OF THE MOLECULAR WEIGHTS OF CERTAIN INNER-COMPLEX COMPOUNDS

In the study of inner-complex compounds, their experimentally determined molecular weights are a very important characteristic. However, cryoscopic and ebullioscopic methods cannot always be applied here, owing to the low solubility of inner-complex compounds in ordinary solvents.

In this case the most convenient proved to be the comparatively recently proposed method for determining molecular weight from absorption spectra, first applied to determine the molecular weights of picrates ([1]), as well as of some other organic and complex compounds ([2,3]). The basis of this method is the proposition that if certain compounds contain the same chromophoric grouping, then the molar absorption coefficient of this chromophoric grouping ε is constant for all substances, whereas the optical density d depends on the molecular weight of the absorbing substance.

Hence, if K'_{ud} and K^x_{ud} are the specific absorption coefficients, then

$$K'_{\text{ud}} = \frac{d'}{C'_{\text{v}} l} \quad \text{and} \quad K^x_{\text{ud}} = \frac{d^x}{C^x_{\text{v}} l},$$

where C'_{v} and C^x_{v} are the weight concentrations in grams per liter; d' and d^x are the optical densities of the solutions; l is the thickness of the absorbing layer. On the other hand, $K'_{\text{ud}} = \frac{\varepsilon'}{M'}$ and $K^x_{\text{ud}} = \frac{\varepsilon^x}{M^x}$, and since $\varepsilon' = \varepsilon^x$, then

$$M^x = M' \frac{K'_{\text{ud}}}{K^x_{\text{ud}}}.$$

Consequently, knowing the weight concentration and the optical density of the absorbing solutions, one can calculate the specific absorption coefficients K_{ud}, and, knowing the molecular weight of one of the substances, determine the molecular weight of the compound under investigation.

In the present article the possibility is considered of applying the spectrophotometric method of determining molecular weights to inner-complex compounds

formed by derivatives of 8-hydroxyquinoline of the Mannich-base type with a series of divalent cations. Extension of this method for determining molecular weight to inner-complex compounds proves possible because the absorption spectra of the inner-complex compounds studied in the wavelength region 290-350 mμ are identical with the absorption spectra of the chelating substances (Mannich bases). As the compound with known molecular weight, in each case we took the 8-hydroxyquinoline derivative with which the complex had been formed. Absorption spectra of solutions in distilled dioxane were recorded on an SF-4 spectrophotometer at room temperature. Since on

Table 1

Molecular weights of the complexes

Name of complex	Formula	Wavelength, mμ	K_{dil} of base	K_{dil} of complex	Calculated Eq. wt.	Mol. wt.	mol. wt.	Error, %
7-(m-nitroanilinobenzyl)-8-hydroxyquinolinate of tungsten	$(C_{22}H_{16}N_3O_3)_2WO_2$	324	100,00	75,00	494,0	988	957	−3,12
7-(m-nitroanilinobenzyl)-8-hydroxyquinolinate of molybdenum	$(C_{22}H_{16}N_3O_3)_2MoO_2$	324	100,00	87,5	424	848	869	+2,41
7-(m-nitroanilinobenzyl)-8-hydroxyquinolinate of copper	$(C_{22}H_{16}N_3O_3)_2Cu$	324	100,00	90,62	409	818	804	−1,74

Name of complex	Formula	Wavelength, mμ	K_{dil} of base	K_{dil} of complex	Eq. wt.	Calculated Mol. wt.	mol. wt.	Error, %
7-(m-nitroanilinobenzyl)-8-hydroxyquinolinate of nickel	$(C_{22}H_{16}N_3O_3)_2Ni$	324	100,00	96,87	396	792	799	+0,87
7-(m-nitroanilinofurfuryl)-8-hydroxyquinolinate of tungsten	$(C_{20}H_{14}N_3O_4)_2WO_2$	300	262,5	197,5	480	960	937	−2,44
7-(m-nitroanilinofurfuryl)-8-hydroxyquinolinate of molybdenum	$(C_{20}H_{14}N_3O_4)_2MoO_2$	300	262,5	216,63	439	878	848	−3,53
7-(o-nitroanilinofurfuryl)-8-hydroxyquinolinate of nickel	$(C_{20}H_{14}N_3O_4)_2Ni$	324	120,6	109,4	398	796	778	−2,31
7-(n-nitroanilinopiperonyl)-8-hydroxyquinolinate of tungsten	$(C_{23}H_{16}N_3O_5)_2WO_2$	298	300,0	237,5	524,7	1049	1043	−0,57

Since the character of the substituent influences the absorption spectra of the Mannich bases, for each Mannich base and the complexes formed with it the

optical density was measured at a correspondingly selected wavelength. Since the composition of the inner-complex compound is generally expressed by the formula $Me(OM)_2$, where HOM is a molecule of the Mannich base, only the equivalent weight was determined. The calculation formula for determining the molecular weight takes the form:

$$M^K = 2\left[(M^{\text{base}} - 1)\,\frac{K_{\text{dil}}^{\text{base}}}{K_{\text{dil}}^{K}}\right].$$

The results obtained are given in Table 1.

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Note: Figure translations are in progress. See original paper for figures.