The Application of the Dielectric Constant Measurements to Determination of the Hydrogen-Bond Energy of Hydrophobic Organic Compounds

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Received September 24, 1976

Infrared absorption spectroscopy belongs to these analytical methods, which have wide application in estimating hydrogen-bond energies *(1)*. In the present paper an effort was undertaken to apply the dielectric constant measurements to evaluate the mean hydrogen-bond energy levels of some selected homologous groups of chemical compounds. The chemical compounds examined in our experiment were higher fatty alcohols and acids, which showed hydrophobic properties.

EXPERIMENTAL

The samples of chemical reagents used in our investigations were lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol, eicosyl alcohol, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, and the following bicomponent systems: lauryl alcohol–stearyl alcohol and stearyl alcohol–lauric acid, in which the molecular fraction ratios of the components were successively 0.8: 0.2, 0.6 : 0.4, 0.4 : 0.6, and 0.2 : 0.8.

The above samples were examined by dielectric and spectroscopic measurements.

The dielectric constant measurements were performed with the help of the model OH-302 Radelkis decameter (product of Hungary). The dielectric constant values were determined at the melting points of the discussed samples. The range of the measurement error was always below ±0.5%.

The IR spectra were run with the help of the model Specord 71 IR spectrophotometer (Carl Zeiss Jena, East Germany) in the range of 4000 to 2000 cm^{-1}. The measurements were performed for the solutions of the examined samples in carbon tetrachloride (spectroscopic grade); the concentration of these solutions was 0.50, 0.25, and 0.125 mol/liter, and the cell paths were 0.16, 0.40, and 1.00 mm, respectively. The spectroscopic cell windows were made of NaCl. The IR spectra were run in the temperature range 20–60°C (three measurements at 20, 40, and 60°C), and the

ΔH values were calculated, which according to our unpublished results (2) reflect the equilibrium states between linear and cyclic forms of associates. For the sake of simplicity we call these ΔH values the mean hydrogen-bond energy levels, although the proper definition is not given here. Because of the partial interference of the C–H valence vibrational bands with the similar band of the associated O–H group, belonging to the aliphatic acids, the thermodynamic evaluations concerning this group of compounds were partially eclipsed by the comparatively high error of ± 1 kcal/mol. With alcohols the analytical error achieves the level of ± 0.7 kcal/mol.

RESULTS

On the basis of the mean hydrogen-bond energy values, which were determined for the alcohols, acids, and bicomponent systems, and of the dielectric constant values an effort was made to formulate the empirical dependence between the mean hydrogen-bond energy levels and those of the dielectric constant. The simplest way to present this dependence may be as follows:

$$\Delta H = A \times R \times \epsilon,$$

where ΔH is the mean hydrogen-bond energy of the tested sample (cal/mol), R is the gaseous constant (1.986 cal/mol $\times$ $^{\circ}K$), ϵ is the dielectric constant, and A is the constant value, which characterizes the given homologous group of substances ($^{\circ}K$); its physical meaning is not discussed in the present paper.

The results of our experiments are shown in Tables 1–4. The results of the hydrogen-bond energy evaluations, obtained on the basis of the IR spectroscopic method, were compared with these, based on the empirical equation.

TABLE 1

THE MEAN HYDROGEN-BOND ENERGY LEVELS FOR THE HOMOLOGOUS
GROUP OF ALCOHOLS, CALCULATED ON THE
BASIS OF THE IR SPECTROSCOPIC RESULTS
AND FROM THE EMPIRICAL EQUATION[a]

Chemical compound	The dielectric constant value ϵ	ΔH (kcal/mol)	
		From IR	From equation
Lauryl alcohol	5.28	6.7	6.7
Myristyl alcohol	3.71	5.0	4.8
Palmityl alcohol	3.50	4.6	4.5
Stearyl alcohol	3.29	4.4	4.2
Eicosyl alcohol	2.99	3.2	3.9

[a] The A value with the examined homologous group of hydrophobic fatty alcohols equals 650° K.

TABLE 2

THE MEAN HYDROGEN-BOND ENERGY LEVELS FOR THE HOMOLOGOUS GROUP OF ACIDS,
CALCULATED ON THE BASIS OF THE IR SPECTROSCOPIC
RESULTS AND FROM THE EMPIRICAL EQUATION[a]

Chemical compound	The dielectric constant value, ϵ	ΔH (kcal/mol)	
		From IR	From equation
Lauric acid	2.43	8.4	8.4
Myristic acid	2.34	8.0	8.1
Palmitic acid	2.30	7.3	7.9
Stearic acid	2.29	6.9	7.8
Arachidic acid	2.28	5.0	7.7

[a] The A value with the examined homologous group of hydrophobic fatty acids equals 1750 °K.

TABLE 3

THE MEAN HYDROGEN-BOND ENERGY LEVELS FOR THE LAURYL ALCOHOL–STEARYL
ALCOHOL SYSTEM, CALCULATED ON THE BASIS OF THE IR SPECTROSCOPIC
RESULTS AND FROM THE EMPIRICAL EQUATION

The bicomponent system	The molecular fraction ratio of the components	The dielectric constant value, ϵ	ΔH (kcal/mol)	
			From IR	From equation
Lauryl alcohol:	1.0 : 0	5.28	6.7	6.7
stearyl alcohol	0.8 : 0.2	4.59	6.0	5.9
	0.6 : 0.4	3.68	4.9	4.8
	0.4 : 0.6	3.46	4.5	4.5
	0.2 : 0.8	3.31	4.4	4.3
	0 : 1.0	3.29	4.4	4.2

As was shown in Tables 1–4, there is a significant resemblance between the results of the measurements obtained from the spectroscopic and dielectric methods. However, the results derived from the spectroscopic data include a comparatively high error; nevertheless, their differentiation, especially with the extreme representatives of the homologous group of alcohols, greatly surpasses the error of the applied method. Because of this, as well as the fact that with the alcohols the higher accuracy of the IR spectra evaluation could have been achieved, the better accuracy of the number value of the A constant was achieved, facilitating good conformity and applicability of the empirical equation.

With the homologous group of acids there was greater difficulty in estimating the respective IR spectra, which resulted in less accurate evaluations. The eventual use of the homologous group of the same acids with the deuterated aliphatic chain might help to obtain a better accuracy.

TABLE 4

THE MEAN HYDROGEN-BOND ENERGY LEVELS FOR THE STEARYL
ALCOHOL–LAURIC ACID SYSTEM, CALCULATED ON THE
BASIS OF THE IR SPECTROSCOPIC RESULTS AND
FROM THE EMPIRICAL EQUATION[a]

The bicomponent system	The molecular fraction ratio of the components	The dielectric constant value, ϵ	ΔH (kcal/mol)	
			From IR	From equation
Stearyl alcohol:	1.0 : 0	3.29	4.4	4.2
lauric acid	0.8 : 0.2	3.02	5.4	5.2
	0.6 : 0.4	2.84	6.1	6.1
	0.4 : 0.6	2.72	7.0	7.1
	0.2 : 0.8	2.54	—	7.7
	0 : 1.0	2.43	8.4	8.4

[a] In this case, in the equation $\Delta H = A \times R \times \epsilon$, the A parameter was replaced by the $650 \times N_{Alc} + 1750 \times N_{Ac}$ (°K) expression; N_{Alc}–the molecular fraction of the alcohol; N_{Ac} –the molecular fraction of the acid.

Nevertheless, the general statement can be made that with the chosen groups of hydrophobic aliphatic alcohols and acids, a definite counter-dependence exists between the dielectric constant values and the mean energetic level of the hydrogen bonds present in these compounds.

REFERENCES

1. Pimentel, G. C., and McClellan, A. C., "The Hydrogen Bond," Freeman, San Fran-
   cisco, 1960, Chap. 3.
2. Sliwiok, J., and Kowalska, T., unpublished results.