Molecular-weight Determination by the Vapor-pressure-Depression Method using Gas Chromatography[1)]

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The molecular-weight-determination method based on the principle of vapor-pressure depression has not been widely utilized because of the difficulty of measuring precisely small differences in the vapor pressure. Now, however, we have been able to measure conveniently the degree of vapor-pressure depression of the solution by means of gas chromatography and determine the molecular weight of the solute within an error of 3%.

The method and the obtained results will be reported here.

According to Raoult's law, the degree of the depression of the solvent vapor in a dilute solution is equal to the mole fraction of the solute. The next equation is thus obtained:

$$(p^\circ - p)/p^\circ = n/(N+n) \qquad (1)$$

$p^\circ =$ vapor pressure of a pure solvent
$p =$ vapor pressure of the solvent in the solution
$n =$ mole number of the solute dissolved in N mol of the solvent

When w grams of a solute is dissolved in W grams of a solvent with a molecular weight of M, the term of $(p^\circ - p)/p^\circ$ can be calculated from the peak height of the chromatograms of the pure solvent (h°) and the solvent in the solution (h).

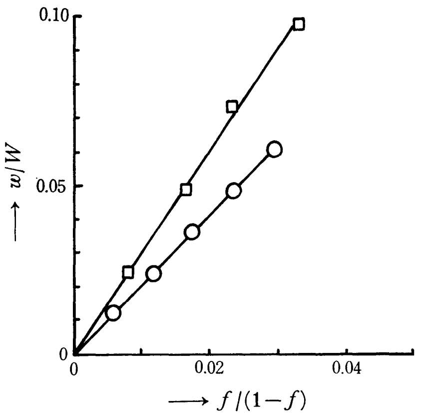

Fig. 1. Relation of molality and depression degree of vapor pressure of benzoic acid in acetone and benzene solution.
○ Benzoic acid in acetone solution
□ Benzoic acid in benzene solution

TABLE 1. MOLECULAR WEIGHT DATA DETERMINED BY VAPOR PRESSURE DEPRESSION METHOD

Solute	Solvent	Experimental value	Theoretical value	Error (%)
Naphthalene	Acetone	128.52	128.17	0.27
	Benzene	127.58		0.46
	Carbon tetrachloride	128.66		0.38
	Ethyl alcohol	130.94		2.16
Benzoic acid	Acetone	123.42	122.12	1.06
	Benzene	236.85*	*dimer 244.24	3.03
	Carbon tetrachloride	234.78*		3.87
	Ethyl alcohol	125.65		2.89
Dipyridin-coppernitrate	Acetone	344.18	345.76	0.46
Benzene	Toluene	79.65	78.11	1.97
n-Hexane	n-Heptane	86.39	86.18	0.24
Carbon tetrachloride	Toluene	155.62	153.82	1.17

Hence, the molecular weight of the solute, m, is obtained using this equation:

$$m = w \cdot M/W[1-(h^\circ - h)/h^\circ \, / \, (h^\circ - h)/h^\circ] \qquad (2)$$

Equation (2) can then be transformed to the next equation when $(h^\circ - h)/h^\circ$ is represented as f:

$$m/M = w/W/f/(1-f) \qquad (2)'$$

In Fig. 1, the concentration of each solution (w/W) *vs.* $f/(1-f)$ is plotted. From this slope ($=m$/M) of the plot, the molecular weight of the solute can be calculated.

The obtained results are shown in Table 1.

In this experiment, the vapor of a pure solvent or solution was saturated in a glass flask at a constant temperature slightly lower than room temperature. A Teflon stopper was used for this flask. A glass syringe and a stainless-steel pipe were attached to this stopper; the fromer was used for pushing out the sample gas in the flask, while the latter was used for introducing the sample vapor to the gas sampler of the gas chromatograph.

The concentration of the solution used was higher than 0.05 molality. Now, an experiment on the solution of less than 0.05 molality is in progress.

1) A part of this work was presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.