

Molecular Weight Determination in Aqueous and Nonaqueous Solvents II. Thermodynamic Properties of Various Solvents

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The change in the resistance of a thermistor from its value when surrounded by a pure solvent is plotted against the concentration of solutions substituted for the solvent. The solutes are chosen for stability and freedom from tendency to associate or dissociate in order to establish a calibration curve for the determination of molecular weights. Within the limit of experimental error, the curves appear to be straight lines in dilute solutions. The slopes of these lines may be used to estimate the approximate thermodynamic properties of solvents by methods analogous to those used in boiling point elevation studies.

THE THERMOELECTRIC vapor-phase osmometer formerly used to study colligative properties of various solutes (1) was improved upon by its developers (2) in a later study of molecular weight determination. This improved instrument has been used to measure changes in the resistance of a thermistor in contact successively with pure solvent and dilute solutions. A matching thermistor in contact with pure solvent during each measurement was used as a reference. The solutes were carefully selected for stability and freedom from tendency to associate or dissociate, and solutions measured ranged in concentration from 0.01 to 0.2 molal. These resistance changes plotted against their respective concentrations give, for each different solvent, a calibration curve that is used for the determination of the molecular weights of solutes. Within the limit of experimental error, these curves appear to be straight lines. The slopes of these lines are shown to be related to thermodynamic properties of certain solvents. The use of equations derived on the assumption of equilibrium show to a very good approximation that these results may be treated like boiling point elevation data at room temperature.

The aforementioned instrument (2) consists of a Wheatstone bridge circuit containing a pair of 100,000 ohm thermistors, a recording potentiometer, and a temperature control system. The measuring thermistor is in series with a decade resistance box which is used to balance the bridge. These thermistors have a high negative temperature coefficient of resistance of about 4% or 4000 ohms/1°C. Instrument sensitivity is such that a change in resistance of less than 1 ohm may be observed. Therefore, a temperature change of approximately $2 \times 10^{-4}^\circ$ can be observed. Each thermistor is housed in a separate glass cell which is lined with platinum gauze. This gauze, when wet with solvent, provides an atmosphere of solvent vapor inside the cell. Using a ground-glass tipped medicine

dropper, drops of solution are placed on the thermistor tip *via* a capillary tube. Following each measurement, the drop of solution is rinsed from the thermistor tip with several successive solvent washings. A lower reservoir and ejection capillary allow for the removal of this waste material.

Both cells are immersed in a constant-temperature bath maintained at $25.00^\circ \pm 0.005^\circ$ by the temperature control system, involving a water bath in a Dewar flask controlled by an Electron-o-therm Sr., model 148, Technical Equipment Co., Walnut Creek, Calif. The entire apparatus is maintained in a constant-temperature controlled atmosphere of a closed cabinet.

One thermistor, wet with a drop of solvent, is always used as a reference resistor. The second holds the various solutions under study including the solvent as the initial calibrating drop. The thermistors measure a slight increase in temperature caused by condensation of the solvent vapor upon the drop of solution, which has a lower vapor pressure. This process in turn changes the resistance of the thermistor in question causing an off-balance condition across the bridge. The recording potentiometer measurement of the off-balance condition is directly related to the change in resistance necessary to return the bridge to balance. The resistance so indicated is added to the decade box in series with the sample thermistor. The difference between this reading and the initial reading of the same box when pure solvent was on the thermistor is the " ΔR " value that is required for the calculations.

EXPERIMENTAL

Five solvents selected for study were water, 95% ethanol, benzene, ethyl ether, and carbon tetrachloride, while sucrose and benzil were the solutes

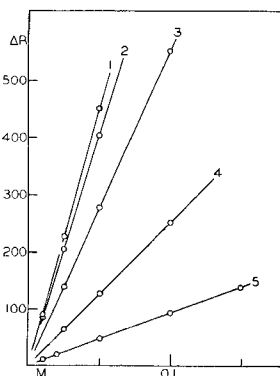


Fig. 1—Calibration curves. Key: 1, carbon tetrachloride; 2, ethyl ether; 3, benzene; 4, 95% ethanol; 5, water. ΔR (ohms) vs. molal concentrations.

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Previous paper: Goyan, F. M., and Johnson, R. D., *J. Pharm. Sci.*, 53, 328(1964).

TABLE I—AVERAGE RESISTANCES AND CONCENTRATIONS FOR SOLUTIONS STUDIED

Substance	No.	Concn., molal	Average ΔR , ohms
Sucrose (in water)	5	0.01	9
		0.02	18
		0.05	46
		0.10	92
		0.15	138
Benzil (in 95% ethanol)	4	0.025	63
		0.05	126
		0.10	252
		0.20	184
Benzil (in benzene)	3	0.025	138
		0.05	277
		0.10	554
Benzil (in ether)	2	0.01	85
		0.025	205
		0.05	404
Benzil (in carbon tetrachloride)	1	0.01	89
		0.025	227
		0.05	452

employed. The organic solvents were all of reagent quality, the benzene being toluene-free. Ordinary distilled water was used. Sucrose and benzil were also of reagent quality, and purification procedures included recrystallization of the benzil from absolute alcohol and sucrose from water.

Several concentrations of solutions were prepared for each solvent between the range of 0.01–0.2 molal. The solutes were weighed out accurately using an analytical balance, placed in a tared flask, and proper solvent added by weight to give the desired w/w solutions. ΔR readings were obtained as previously described, and a weighted average value was computed for each concentration. These values were plotted against their respective molal concentrations, and the slopes of the curves computed.

RESULTS

Figure 1 and Table I show the results obtained for the various solvents under study. The data for benzene appear in an earlier paper (2), and most of the other data were presented in the doctoral thesis of one of the authors (3). However, the values for 95% ethanol represent later work. The slopes of the curves in Fig. 1 and their reciprocal values have been tabulated in Table II.

DISCUSSION AND RESULTS

From classical thermodynamics the well-known relationship of physical chemistry (4) may be written:

$$\Delta T_b = \frac{RT^2}{l_v \cdot 1000} m \quad (\text{Eq. 1})$$

where ΔT_b is the boiling point elevation, l_v is the latent heat of vaporization in calories per gram, m is the molal concentration, R represents the gas constant, and T is the absolute temperature. The linearity of the results shown in Fig. 1 indicate that ΔR is a colligative property proportional to ΔT_b . Therefore,

$$\Delta R = \frac{K}{l_v} \cdot m \quad (\text{Eq. 2})$$

TABLE II—SLOPES, RECIPROCAL SLOPES, AND LATENT HEATS OF VAPORIZATION CORRESPONDING TO CURVES IN FIG. 1

Curve No.	Solvent	Slope $\left(\frac{dR}{dm}\right) = S$	Reciprocal Slope $1/S$	l_v (cal./Gm. at 25°)
1	CCl ₄	9060	0.110×10^{-3}	50.2
2	Ether	8050	0.124×10^{-3}	86.1
3	Benzene	5540	0.181×10^{-3}	103
4	95% Ethanol	2520	0.397×10^{-3}	224
5	Water	920	1.087×10^{-3}	584

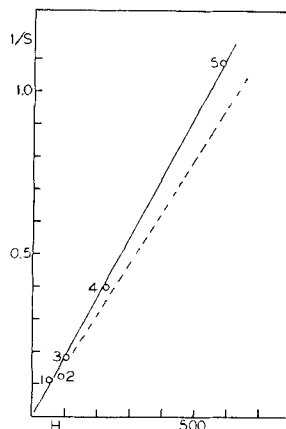


Fig. 2—Reciprocal slopes ($\times 10^3$) of curves of Fig. 1 vs. latent heats of vaporization (cal./Gm.). Numbers correspond to those listed for Fig. 1.

where K is a proportionality constant from whence it follows that:

$$l_v = K \cdot \frac{dm}{d\Delta R} \quad (\text{Eq. 3})$$

$\frac{dm}{d\Delta R}$ represents the reciprocal slopes listed in Table II. These values plotted against the corresponding latent heats of vaporization should give a straight line. Figure 2 shows this graphically. Latent heats of vaporization displayed in Table II were obtained for 25° by graphical interpolation of established values at various temperatures (5). The value for 95% ethanol was calculated for 25° from the value at the boiling point given by Licht and Denzler (6) by assuming that pure ethanol and the azeotrope required the same correction in going from the boiling point to 25°.

It will be noted from Fig. 2 that all of the points are close to the solid straight line. Ether, which seemed to be the most difficult to work with experimentally, comes closer to the theoretical value shown by the dotted line. This line was established by assuming the relationship:

$$\Delta T_b = \Delta R \cdot f \quad (\text{Eq. 4})$$

where ΔT_b and ΔR are taken from Eq. 1, and f represents a conversion factor found to be 2.8×10^{-4} /ohm by direct measurement with a thermometer. Combining Eqs. 1 and 4 and evaluating all terms gives the slope of the dotted line. By the same reasoning, the solid line gives a value for f of 3.26×10^{-4} /ohm.

SUMMARY AND CONCLUSION

Calibration curves described above for determining colligative properties in various solvents may be combined in such a way as to reveal expected thermodynamic properties of the solvents. Measurements made on drops of solutions held on the tips of glass rods containing a thermistor show that the vapor exchange is sufficient to minimize the effect of the heat loss which must occur. This situation is no different in principle from the use of a thermometer in a typical boiling point experiment. Although undoubtedly refinements should include the use of instrument constants accounting for heat

conduction and other factors, the apparent approximate validity of a classical thermodynamic treatment is a good indication of the effectiveness of this particular instrument.

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Absorption and Permeability of a Flavor in Plastic Containers as Determined by Head-Space Gas Chromatography

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When guarana flavor was used as the flavoring agent in an oral preparation and placed in plastic containers, and when head-space gas-liquid chromatography was applied to the investigation of the stability of this product, the method was found to be rapid and specific. The flavoring constituents of guarana were detected as having been absorbed by the wall of the container and having permeated to the atmosphere surrounding the outside surface of polyethylene bottles. Polyvinyl chloride bottles showed definite absorption of guarana and some change in the appearance of the containers but gave no evidence of permeability.

THE INCREASED importance of plastic containers in the packaging industry has emphasized the need for determining their compatibility as a substitute for glass. The object of this work was to develop a rapid method for the study of one phase of this compatibility. Much has been accomplished to improve plastics (1) and this achievement has progressed to the point that plastics almost look like glass. Because of its nonfragile nature, lighter weight, and low production cost there is much interest in the pharmaceutical industry for its use as a substitute for glass. A major problem, that of permeability, is associated with plastics and this has led to some reservation as to their total acceptance. In studies thus far reported in the literature, the observations have been arrived at by noting loss in weight and change in appearance, *i.e.*, swelling or collapse of container (2), these being methods which required long standing, careful weighing and handling, and are useful only on a macro scale. Where very small amounts of flavoring are utilized, the aforementioned approach is ineffective and necessitates another analytical technique. In this laboratory such a technique was devised. The author is now able to detect minute traces of flavors as they become absorbed or permeate into new zones within the plastics by using head-space GLC. The procedure is simple, and the graphs obtained are a permanent record of the observations. The use of head-space GLC has been reported in several publications, especially those pertaining to studies in wine and beer flavor (3, 4). These efforts are merely a continuation of these studies. Since glass is very inert and impermeable,

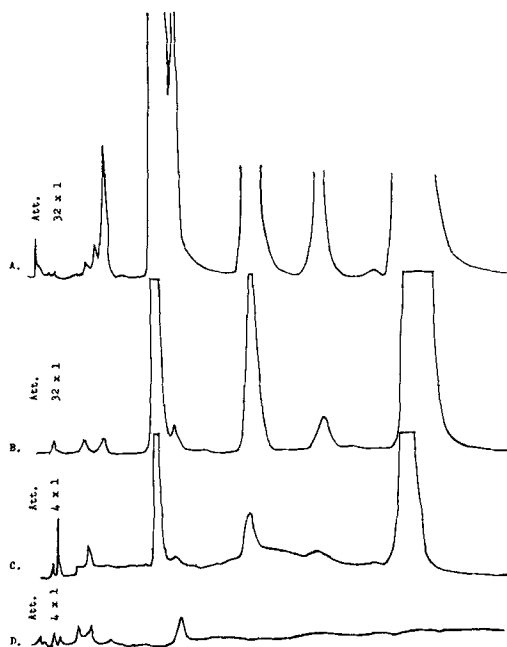


Fig. 1—Head-space gas chromatography of 0.0002% guarana flavor in water. Key: A, air sample above solution of 0.0002% guarana; B, air sample withdrawn from the interior of a washed plastic container that had contained a solution of 0.0002% guarana; C, air sample from a closed glass jar containing a polyethylene bottle filled with the guarana flavor; D, outside surface air adjacent to glass jar containing the guarana flavor (completely comparable to laboratory air).