

Spectral Absorbance of Some Aqueous Solutions in the Range 10° to 40° C

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The effect of temperature upon the absorption spectra in the ultraviolet and part of the visible ranges was determined for several compounds in aqueous solution. Temperatures used were 10°, 25°, and 40° C. The materials used as solutes included both inorganic and organic compounds, namely, potassium nitrate, potassium dichromate, diphenylsulfone, diphenyl phosphate, 4,4'-diaminobenzophenone, and *m*-cresolsulfonphthalein. As the temperature was decreased there was an increase in maximum absorbance of all compounds except in the case of diphenyl phosphate, the behavior of which was anomalous. A slight shift of the absorbance curves also occurred. The relationship between absorbance and temperature was not linear in the temperature range investigated. The results showed that temperature should be controlled within ± 2 deg C if molar absorbance values are to be obtained within 0.5 percent. Temperature coefficients for an individual compound require extensive absorption measurements of that compound in known media, and such coefficients will hold for the specified wavelengths only under specified conditions. As a general guide the temperature should be controlled to ± 0.5 deg C.

1. Introduction

It is well known that the absorption spectra of both organic and inorganic compounds are affected by temperature changes. Too little attention has been given, however, to the extent of these changes.

Among the early workers who studied the effect of temperature upon the absorption spectra of solutions were Jones and Guy and their co-workers [1].¹ They gave a great deal of attention to the behavior of solutions of the rare-earth and other metallic salts in the ultraviolet, visible, and near infrared spectral ranges at temperatures between 20° and 200° F (-6.7° to 93.3° C). Lewis and Calvin [2] reported the results of studies of compounds in ether-alcohol mixtures at very low temperatures. Haupt [3] recently determined the absorption spectrum of potassium dichromate in an aqueous solution at 25° and 50° C, and suggested that it be used as a calibration standard for spectrophotometers. Yarborough, Haskin, and Lambdin [4] also made spectrophotometric measurements on several organic compounds in methanol and iso-octane at different temperatures and determined temperature coefficient over a limited range. Sager and Siewers [5] reported absorbance values, dissociation constants, and related thermodynamic properties of some organic bases derived from spectrophotometric measurements at temperatures from 10° to 40° C.

The purpose of the present work was to determine whether or not a general pattern of spectral absorption behavior could be predicted for certain classes of chemical compounds in solution. A few materials were selected and their absorbance was compared over a range of temperatures from 10° to 40° C. Two inorganic materials of high purity were chosen, namely, potassium nitrate and potassium dichromate. The four organic compounds studied were of relatively simple structure. They were diphenylsulfone, diphenyl phosphate, 4,4'-diaminobenzophenone, and *m*-cresolsulfonphthalein. Spectrophotometric measurements were made of all of these

materials in the ultraviolet from 210 $m\mu$ through 400 $m\mu$. For *m*-cresolsulfonphthalein, which is a hydrogen-ion indicator, measurements were extended to 670 $m\mu$ in the visible range.

2. Equipment

A model DU Beckman spectrophotometer was fitted with a constant-temperature cell compartment of our own design, described earlier [5], and water was circulated through the walls, top, and bottom from a thermostated water-bath. The cell compartment holds two cylindrical absorption cells equipped with removable quartz end-plates of 38-mm diameter. The depth of layer of solution used in these studies was confined to 1 cm. After equilibrium was reached, temperatures within the compartment did not vary more than ± 0.2 deg at 10° and at 40° C, and less than ± 0.1 deg at 25° C, as measured by a thermometer inserted through the top of the compartment box to an air space above the cells.

3. Materials

Potassium nitrate, reagent grade, was recrystallized twice from distilled water and dried in an oven at 110° for 24 hr.

Potassium dichromate, NBS Standard Sample 136, was used without further purification or drying.

Diphenyl phosphate was synthesized by A. A. Maryott of the Physical Chemistry Section. It was recrystallized twice from ethyl alcohol and water, dried in a vacuum oven at 50° C, and kept in a desiccator until used. The melting point was determined as 69° to 70° C.

Diphenylsulfone was obtained from Eastman Kodak Co. It was recrystallized once from ethyl alcohol and again from benzene. The melting point was 128° to 129° C.

4,4'-Diaminobenzophenone was obtained from Eastman Kodak Co. and was recrystallized twice from ethyl alcohol and water. It melted at 236° to 239° C.

m-Cresolsulfonphthalein was especially prepared for this laboratory several years ago by W. A. Taylor & Sons of Baltimore, Md., for studies of ionization constants of indicators. It is difficult to synthesize

¹ Figures in brackets indicate the literature references at the end of this paper.

a pure indicator or dye, but analyses for carbon, hydrogen, and sulfur showed it to be of much greater purity than the usual commercial product.

4. Procedure

Stock solutions of each compound were prepared at 25° C with conductivity water. Further dilutions for the spectrophotometric measurements were made by volumetric procedures with conductivity water, or in cases where it was necessary to control the hydrogen-ion concentration, dilutions were made with acid, base, or buffers.

Before and after each series of observations the absorption cells were calibrated over the spectral range of the absorbing compound, using water in both the solvent and the solution cell. It was usually possible to complete observations on 1 compound within 1 day when the following sequence of temperatures was used: 25°, 10°, 25°, 40°, and 25°. The three sets of readings at 25° gave assurance that no changes had occurred in the solutions during the changing of the temperatures. A period of 30 min was allowed for attainment of equilibrium after the desired temperature was reached.

All results were verified by a second set of observations on freshly prepared solutions. In the case of diphenyl phosphate, 6 series were made: 3 series in water, 1 series in acid, another in phosphate buffer, and another in sodium hydroxide solution.

5. Calculation of Molar Absorbance Values

The law of absorption states that, at any given wavelength,

$$\epsilon = A/bM, \quad (1)$$

where ϵ is the molar absorbance of the compound in solution² (often called extinction coefficient), A is the absorbance of the sample ($-\log_{10}$ of the transmittancy), b is the thickness of the layer of solution in centimeters, and M is the molarity of the solution.

The depth of the solution, which is limited by the length of the absorption cell between the end-plates, is not changed significantly by temperature changes between 10° and 40° C and can be considered constant. The relationship between the molarity at the temperature at which the solution is prepared, M_t , and the molarity at a different temperature, $M_{t'}$, is

$$M_{t'} = M_t(d_{t'}/d_t), \quad (2)$$

where d_t and $d_{t'}$ are the corresponding densities. The data on densities were taken from the tables in International Critical Tables, volume III, p. 54, 79, and 89.

6. Presentation of Data

The curves in figures 1 to 6, inclusive, show the molar absorbances of each solute in the respective solvent as a function of wavelength. The compositions and densities of the solutions are shown in table 1.

² ϵ is used in this paper as the symbol for molar absorbance instead of a_M as in previous papers.

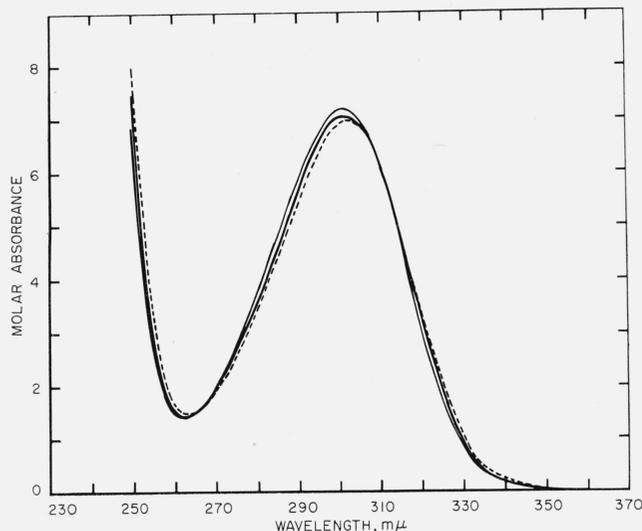


FIGURE 1. *Potassium nitrate in water.*
—, 10° C; — — —, 25° C; ·····, 40° C.

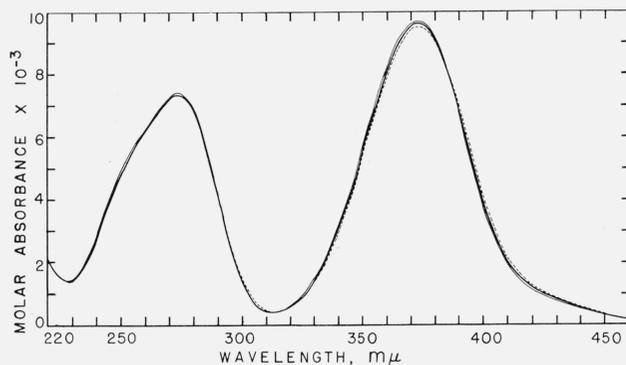


FIGURE 2. *Potassium dichromate in 5 × 10⁻²-M NaOH.*
—, 10° C; — — —, 25° C; ·····, 40° C.

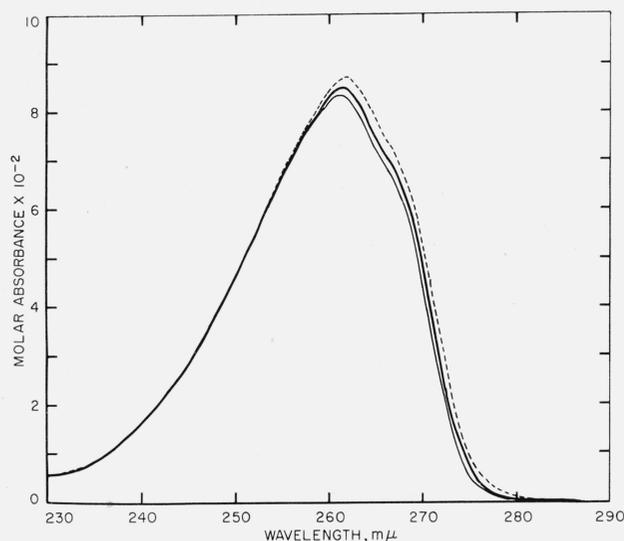


FIGURE 3. *Diphenyl phosphate in water.*
—, 10° C; — — —, 25° C; ·····, 40° C.

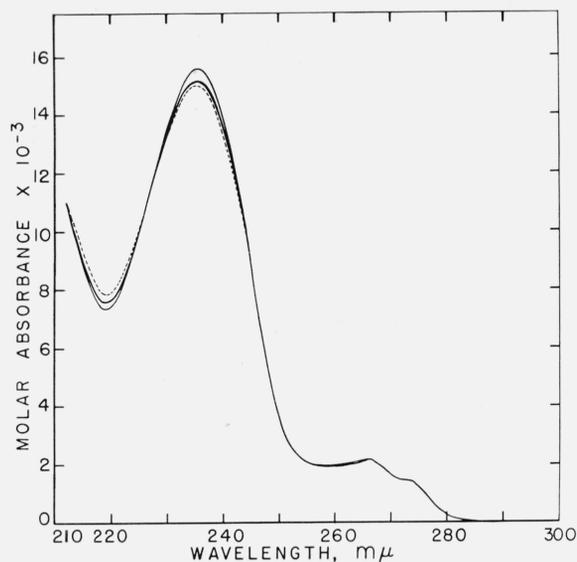


FIGURE 4. *Diphenylsulfone in water.*
 —, 10° C; ---, 25° C; ·····, 40° C.

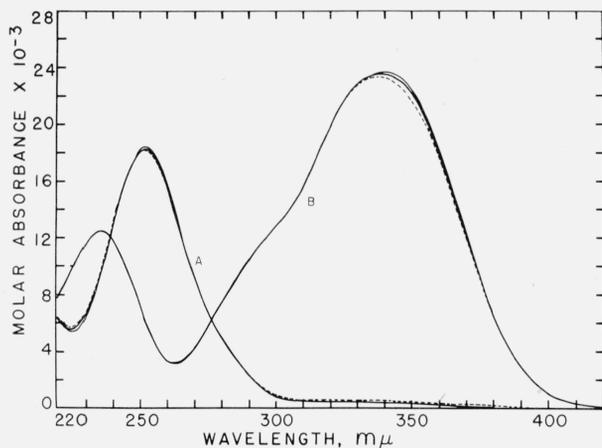


FIGURE 5. *4,4'-Diaminobenzophenone.*

A, Dissociated state in 0.8-*M* HCl; B, undissociated state in 10^{-3} -*M* NaOH.
 —, 10° C; ---, 25° C; ·····, 40° C.

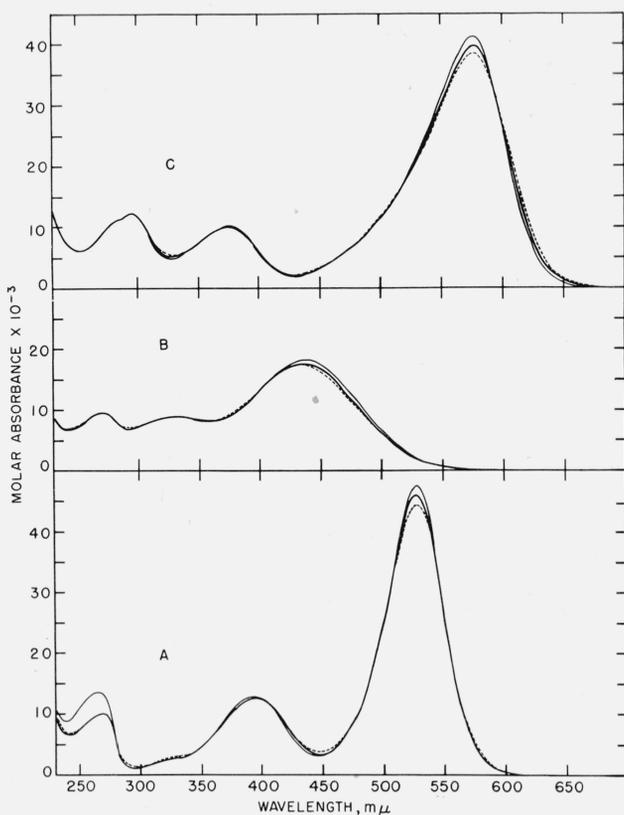


FIGURE 6. *m-Cresolsulphonphthalein.*

A, Red form in 2-*M* HCl; B, yellow form in water; C, purple form in 10^{-1} -*M* NaOH.
 —, 10° C; ---, 25° C; ·····, 40° C.

TABLE 1. *Composition and densities of solutions used for measurement of molar absorbances*

Figure	Solute	Molar concentration of solute	Added acid or base	Molar concentration of added acid or base	Densities at—		
					10° C	25° C	40° C
1	Potassium nitrate	10^{-1}	None		1.0061	1.0032	0.9982
2	Potassium dichromate	6.9×10^{-4}	Sodium hydroxide	5×10^{-2}	1.0023	0.9993	.9945
3	Diphenyl phosphate	7.59×10^{-5}	None		0.9997	.9970	.9922
4	Diphenylsulfone	7.97×10^{-5}	do.		.9997	.9970	.9922
5	4,4'-Diaminobenzophenone	2.47×10^{-5}	Hydrochloric acid	8×10^{-1}	1.0120	1.0088	1.0039
			Sodium hydroxide	10^{-3}	0.9997	0.9970	0.9922
			Hydrochloric acid	2	1.0303	1.0264	1.0211
6	<i>m</i> -Cresolsulphonphthalein	5×10^{-5}	None		0.9997	0.9970	0.9922
			Sodium hydroxide	10^{-1}	1.0046	1.0015	.9967

7. Discussion

In general, aqueous solutions of the compounds studied here show an increase in maximum absorbance as the temperature is decreased, with an accompanying slight shift in the spectral absorption curves. The one exception is diphenyl phosphate which shows a reverse behavior; that is, the maximum absorbance decreases as the temperature decreases. That the conduct of this compound is anomalous was verified by extensive additional absorption data for the compound not only in water but in hydrochloric acid, in phosphate buffer, and in sodium hydroxide solution. The same order of change in the absorbance of diphenyl phosphate held at the different temperatures regardless of the dissolving medium.

In any case, it is obvious that the extent of change in absorbance with change in temperature depends upon the selected wavelength, the largest differences occurring near wavelengths of maximum absorption. Previous workers have found a linear relationship between absorbance values and temperature [3,4]. The results reported here do not show a linear relationship, however.

It would undoubtedly be helpful if observations could be extended further into the ultraviolet region of the spectrum. One is dealing at best with only a partial spectrum due to experimental limitations of the spectrophotometer and to the fact that aqueous media themselves absorb at lower wavelengths. With extended data in the ultraviolet range, a comparison of the areas under the absorption curves at different temperatures might be of value.

Because the density of the medium in which a compound is dissolved changes slightly as the temperature changes, thereby changing the concentration of the solution under observation, the temperature of the solution should always be stated and taken into consideration when calculating molar absorbance values. Errors introduced by slight fluctuations in room temperature while making measurements are probably negligible in much qualitative work. However, in using spectral absorption data for the determination of molar absorbance values, for calculations of any thermodynamic properties, or for analytical or quantitative work of high precision, the temperature should always be controlled.

Temperature coefficients for an individual compound require extensive absorption measurements of that compound in known media, and such coefficients will hold for the specified wavelengths only under specified conditions. As a general guide the temperature should be controlled to ± 0.5 deg C.

8. References

- [1] Harry C. Jones and J. Sam Guy, Carnegie Inst. of Washington, Publication No. 190 (1913).
- [2] Gilbert N. Lewis and M. Calvin, *Chem. Rev.* **25**, 273 (1939).
- [3] Geraldine W. Haupt, *J. Research NBS* **48**, 414 (1952) RP2331.
- [4] V. A. Yarborough, J. F. Haskin, and W. J. Lambdin, *Anal. Chem.* **26**, 1576 (1954).
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