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Thermal Properties of Aqueous Solutions of Polyvinylpyrrolidone in the Temperature Range 20–80°C

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The thermal properties (thermal diffusivity a, thermal conductivity λ, and volumetric heat capacity ρC_p) of aqueous solutions of polyvinylpyrrolidone (PVP) were measured in the temperature range 20–80°C. The measurements were carried out using the hot-wire (strip) technique. Three different average molecular weights of PVP were used [$M = 10{,}000$ (PVP-10), $M = 24{,}500$ (PVP-24.5), and $M = 40{,}000$ (PVP-40)], i.e., the average degrees of polymerization are 90, 220, and 360, respectively. The results show that the values of the thermal properties depend on the temperature and the concentration of PVP in the medium. The mechanism of heat transfer was discussed. The role of convection and radiation were taken into consideration.

KEY WORDS: heat capacity; hot-wire technique; polyvinylpyrrolidone; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

The present work represents an investigation of thermal properties (λ, a, and ρC_p) of polyvinylpyrrolidone in the temperature range 20–80°C. Three different average molecular weights were used. Since these properties are not yet studied in the measured temperature range, measurement of the thermal properties of the above-mentioned material at various temperatures and concentrations will help the understanding of the heat conduction mechanism in these materials.

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2. EXPERIMENTAL SETUP

An experimental setup for the simultanous absolute measurement of the thermal activity b, thermal diffusivity a, and volumetric heat capacity ρC_p of nonconducting liquids with the AC heated-wire (strip) technique is used [1]. The theory of the plane temperature wave method for determining the thermal activity $b = \lambda/a^{1/2}$ of the investigated liquid combined with the radial heat flow method is used for determining the thermal diffusivity a of a liquids. As a result of this combination all the thermal properties of liquids were determined.

A metallic foil is immersed in the liquid under investigation to produce a plane temperature wave. The foil is heated by means of an alternating current with angular frequency w.

The amplitude of temperature oscillation (θ_0) of a strip is related to the thermal activity of the investigated liquid according to the following formula:

$$b = \frac{d}{2}\left[\frac{1}{2}\left(\frac{W_0}{d\sqrt{w}\,S\theta_0}\right)^2 - 1\right]^{1/2} - 1 \tag{1}$$

where $d = \sqrt{w}\,(\rho C_p)_s h$, W_0 is the power, S is the area of one side of the strip, $(\rho C_p)_s$ is the heat capacity of the strip material, and h is the thickness of the strip.

The amplitude of temperature oscillations (θ) of the wire is related to the thermal properties of the liquid and the wire heat capacity $(\rho C_p)_s$ according to the following relation:

$$\theta = \theta_0\left(\frac{\mathrm{her}^2(X) + \mathrm{hei}^2(X)}{\{X\eta\,\mathrm{hei}(X) + \mathrm{her}'(X)\}^2 + [X\eta\,\mathrm{her}(X) - \mathrm{hei}'(X)]^2}\right)^{1/2} \tag{2}$$

where $X = \sqrt{(2w/a)}\,r$, $\eta = (\rho C_p)_s/(2\rho C_p)_1$, r is the radius of the wire, ρ is the density, θ_0 is the amplitude of the temperature oscillations of a noninertial strip and her, hei, her′, and hei′ are Hankel functions and derivatives. From Eqs. (1) and (2) a, λ, and ρC_p of liquid under investigation can be calculated.

In this technique, the temperature oscillation field can be confined around the sensor in a liquid layer thin enough to suppress the hydrodynamic currents. This eliminates the convective heat transport. The calculated systematic errors of the thermal activity measurements could reach 1.5% for a strip and 2% for a wire. For thermal diffusivity and heat capacity coefficients, these errors are not more 2.5%. Maximum errors for the thermal conductivity measurements were 2.2%.

3. RESULTS AND DISCUSSION

3.1. Volumetric Heat Capacity ρC_p

The results of the measurements of the volumetric heat capacity ρC_p with temperature of polyvinylpyrrolidone (PVP-10) is shown in Fig. 1. The variation of different concentrations of PVP-10 in distilled water (0.5, 1.0, 3.0, and 5.0%) are shown in the same figure. It was found that as the concentration of (PVP-10) increases, the volumetric heat capacity decreases. The decrease in ρC_p can be discussed as the increase in density of the aqueous solution with temperature. The volumetric heat capacity of (PVP-24.5) and (PVP-40) is shown in Figs. 2 and 3. The same behavior is noticed for the two concentrations.

Figure 4 shows the variation of ρC_p of (PVP-40) with different concentrations: 0.5, 1.0, 3.0, and 5.0% at 40°C. From the curve, it was found that as the concentration of PVP increases, ρC_p decreases, which is due to the effect of neighboring atoms. This is believed to be due to a decrease in the density of transverse vibrations that results from higher concentration of PVP.

3.2. Thermal Conductivity λ

Figures 5, 6, and 7 show the variation of λ with temperature for (PVP-10), (PVP-24.5), and (PVP-40) with different concentrations; 0.5, 1.0, 3.0, and 5.0%. The higher is the PVP percentage, the lower is the value

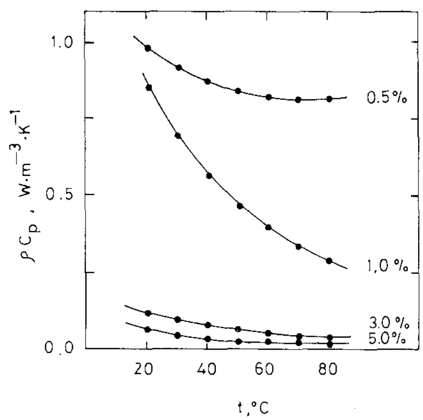

Fig. 1. Variation of volumetric heat capacity with temperature of aqueous solutions of polyvinylpyrrolidone (PVP-10).

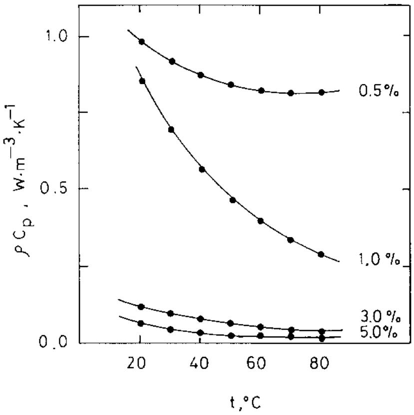

Fig. 2. Variation of volumetric heat capacity with temperature of aqueous solutions of polyvinylpyrrolidone (PVP-24.5).

of λ. The decrease in λ with concentration is related to the decrease in the mean free path of PVP molecules. The relation between the concentration of (PVP-40) and the thermal conductivity λ is shown in Fig. 8. As the concentration increases the viscosity increases and this leads to a decrease in λ according to the following equation reported previously by Berman [2]:

$$\eta\lambda = \text{constant} \tag{3}$$

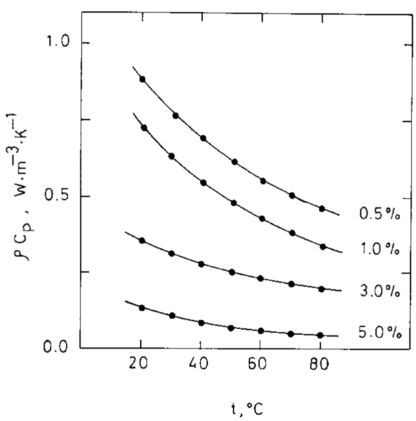

Fig. 3. Variation of volumetric heat capacity with temperature of aqueous solutions of polyvinylpyrrolidone (PVP-40).

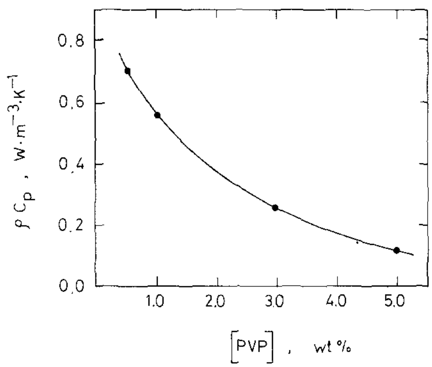

Fig. 4. Variation of heat capacity for different concentrations of polyvinylpyrrolidone (PVP-40) at 40°C.

where η is the viscosity of the investigated liquid. The obtained values of thermal conductivity depend mainly on the molecular weight of the investigated material.

The mechanism of heat transfer in liquids is complicated because of the presence of convective and radiative heat transport accompanying the conduction process. In the present work, great attention was paid to checking for the presence of convection. The thickness of the effective layer L around the sensor immersed in the investigated liquid parallel to the heating source can be calculated from the equation:

$$L = \left(\frac{a}{w}\right)^{1/2} \tag{4}$$

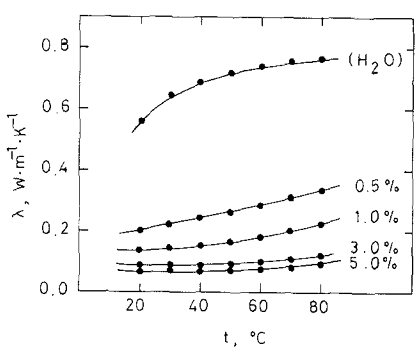

Fig. 5. Variation of thermal conductivity of polyvinylpyrrolidone (PVP-10) with temperature.

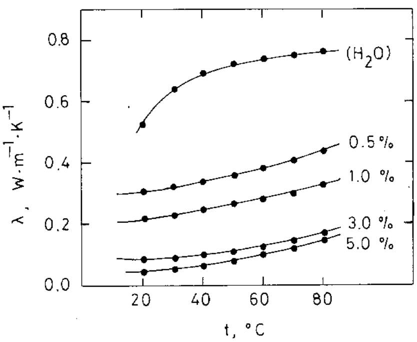

Fig. 6. Variation of thermal conductivity of polyvinylpyrrolidone (PVP-24.5) with temperature.

where w is the angular frequency of heat input. From Table I, it was found that the thickness of the effective layer is sufficiently small to suppress convection.

Since we are concerned only with the measurement of the amplitude of the temperature oscillations, the following formula (derived by Poltz [3] and Schatz and Simmons [4] for the steady-state parallel plate apparatus) can be used to estimate the radiative component of the thermal conductivity coefficient λ_r as follows:

$$\lambda_r = \frac{16}{3}\,\sigma n^2 T^3 \phi(\alpha, L) \tag{5}$$

where σ is the Stefan–Boltzmann constant, n is the refractive index of the liquid, α is the absorption coefficient of the liquid, T is the mean temperature of the liquid, and $\phi(\alpha, L)$ is a compound function, which accounts for the propagation of radiation in an absorping medium and is

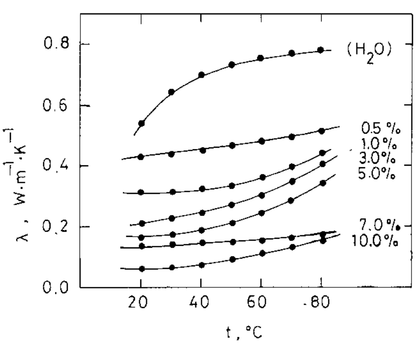

Fig. 7. Variation of thermal conductivity of polyvinylpyrrolidone (PVP-40) with temperature.

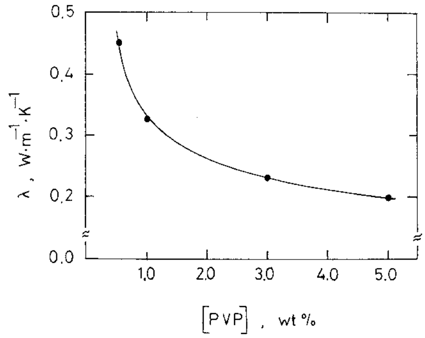

Fig. 8. Relation between the thermal conductivity and different concentrations of polyvinylpyrrolidone (PVP-40) at 40°C.

Table I. The Effective Thickness L of Polyvinylpyrrolidone at 80°C for concentrations of 0.5 and 5.0 wt %

Substance	L (cm) At 0.5 wt %	L (cm) At 5 wt %
(PVP-10)	8.70×10^{-3}	0.040
(PVP-24.5)	8.89×10^{-3}	0.044
(PVP-40)	7.74×10^{-3}	0.044

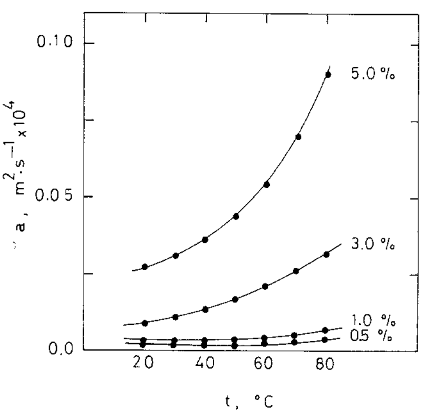

Fig. 9. Dependence of thermal diffusivity of aqueous solutions of polyvinylpyrrolidone (PVP-10) on temperature.

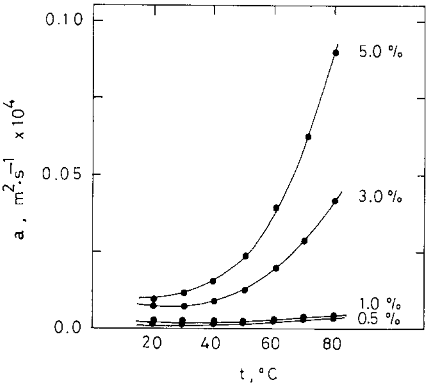

Fig. 10. Dependence of thermal diffusivity of aqueous solutions of polyvinylpyrrolidone (PVP-24.5) on temperature.

given in Ref. 4 as a function of (α, L) with the reflection coefficient of the walls as a parameter. Moreover, this formula can be used when the optical absorption coefficient αL of the investigated liquid is equal to or less than unity ($\alpha L \leqslant 1$), the condition which is fulfilled in this experiment. Therefore, we can conclude that the heat conduction mechanism of the PVP-10, PVP-24.5, and PVP-40 in aqueous solution is due to conduction only.

3.3. Thermal Diffusivity *a*

Variation of the thermal diffusivity a of the above mentioned materials with temperature is shown in Figs. 9, 10, and 11. It was found that a

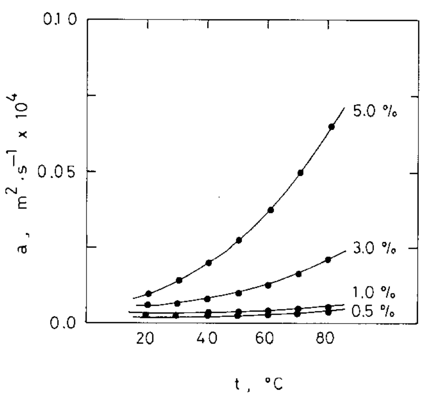

Fig. 11. Dependence of thermal diffusivity of aqueous solutions of polyvinylpyrrolidone (PVP-40) on temperature.

increases as the temperature increases. Also, the thermal diffusivity a increases as the concentration of PVP increases. The thermal diffusivity is related to the thermal conductivity by the relation.

$$a = \lambda / \rho C_{\mathrm{p}} \tag{6}$$

where ρ is the density of the aqueous solution. From this relation we can conclude that the increase in a is due to an increase in λ and decrease in ρC_{p}.

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