Journal of Thermal Analysis, Vol. 53 (1998) 855-859

DETERMINATION OF THE CONCENTRATIONS OF BINARY MIXTURES OF GLYCERINE AND WATER BY A TRANSIENT METHOD

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Abstract

The conductivities of binary mixtures of glycerine and water were measured at 20°C by means of a transient method. The equation describing the correlation between concentration and thermal conductivity was determined. The equation can be used for determining concentrations in mixtures. The results show that (1) the error in the determination of the molar concentration of water in mixtures is less than 1%, (2) the time of measurement is 1 s, (3) this method can be used for on-line analysis in production control.

Keywords: binary mixture, concentration, glycerine-water, on-line analysis, thermal analysis, thermal conductivity

Introduction

Chemical analysis is based on the different physical or chemical properties of different matters. Thermal conductivity is one of the most sensitive physical properties. The determination of the molar concentration (x) of water in binary mixtures of glycerine and water based on the measurement of the thermal conductivity (λ) of the mixture has never been reported. In continuation of our studies on the transient method [1–3] and its application, we now report on the methods and results of estimating the molar concentration (x) through measurement of the thermal conductivity (λ) of the mixture.

Experimental and results

The experimental apparatus and procedure used in the present study were almost the same as described in a previous paper [1]. A specially made small bead of glass thermistor is used as the heating element. It is immersed in the liquid to be investigated. The thermistor is connected to the electric circuit of an unbalance bridge. A rate of voltage change of the bridge, Si, is determined in the ex-

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1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

periment. In this apparatus, *Si* will be inversely proportional to the thermal conductivity of the liquids tested [2, 3].

In order to measure λ of glycerine-water binary mixtures, the apparatus was calibrated at 20°C by using five reference liquids with known thermal conductivities: water (I), 20% methanol (II), 20% ethanol (III), 40% ethanol (IV) and glycerine (V). Figure 1 shows a typical plot of λ *vs.* *Si* for five reference liquids.

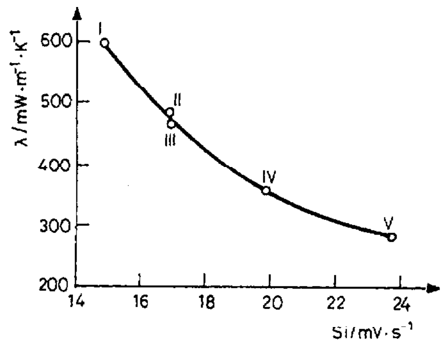

Fig. 1 The plot of λ *vs.* *Si* of five reference liquids I–V at 20°C

The corresponding data were calculated by least-squares method. When the range of λ was between 90–200 mW m^{-1} K^{-1}, we obtained a first power equation [1]. When the range was 280–670 mW m^{-1} K^{-1}, we obtained a calibration equation of the apparatus in the second power:

$$\lambda/\text{mW m}^{-1}\text{ K}^{-1} = 2219.55 - 155.714Si + 3.124Si^2 \quad (1)$$

The average error is less than 1%.

The thermal conductivities of binary mixtures of glycerine and water in four different concentrations at 20°C were measured by means of the calibrated apparatus. The results are shown in Table 1. The plots of λ and *Si* *vs.* *x* obtained from the data in Table 1 are shown in Figs 2 and 3, respectively.

Table 1 Values of *Si* and λ of glycerine-water mixtures at 20°C

x	Si/mV s^{-1}	λ/mW m^{-1} K^{-1}
0	23.728	283.4
0.2	23.202	288.2
0.4	22.705	294.3
0.6	21.425	317.2
0.8	19.250	379.5
1	14.829	597.3

x – molar concentration of water in the mixtures

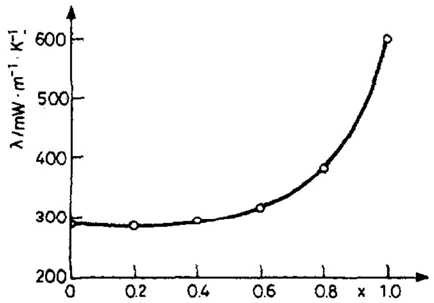

Fig. 2 Plot of λ *vs.* x for glycerine-water mixtures at 20°C

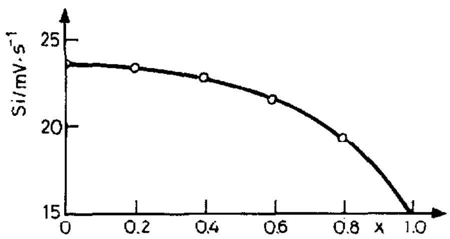

Fig. 3 Plot of Si *vs.* x for glycerine-water mixtures at 20°C

The curves in Figs 2 and 3 can be described using the following expressions:

$$\lambda = 283.40 + 124.11x - 996.2x^2 + 3251x^3 - 4315x^4 + 2250x^5 \quad (2)$$

$$Si = 23.73 - 6.87x + 38.73x^2 - 109.48x^3 + 119.2x^4 - 50.5x^5 \quad (3)$$

To verify the reliability of the determination of x in binary mixtures via Eq. (3) (method I) or Eqs (1) and (2) (method II), we measured two mixtures of glycerine and water under the same experimental conditions as those applied in establishing Eqs (1)–(3) and obtained their values of Si. The experimental data and calculated results are shown in Table 2. From Table 2 it can be seen that (1) the deviation of method II is greater than that of method I, (2) the error in the determination of x by methods I and II is less than 1%.

Error analysis

Error analysis of method I

From Eq. (3) we obtain

$$\frac{\Delta Si}{\Delta x} = |-6.87 + 38.73 \cdot 2x - 109.48 \cdot 3x^2 + 119.2 \cdot 4x^3 - 50.5 \cdot 5x^4|$$

Table 2 Molar concentrations of water in two mixtures

Sample	Si/mV s^{-1}	λ/mW m^{-1} K^{-1}	x	x_f	dev./%
1	17.514		0.8996	0.9011	0.2
		450.5	0.8949	0.9011	0.7
2	22.740		0.3918	0.3905	0.3
		293.8	0.3928	0.3905	0.8

x_f – real molar concentration of water

$\text{dev.} = \frac{|x - x_f|}{x_f}$

where ΔSi is the error in the measurement of Si. The value of ΔSi is obtained as

$$\Delta Si = \sqrt{\frac{\Sigma dSi^2}{n(n-1)}}$$

In a previous paper [1], the value of ΔSi was found to be about 0.01 for toluene. When x=0.4

$$\Delta x = \frac{0.01}{4.44} = 0.002$$

$$\frac{\Delta x}{x} = \frac{0.002}{0.4} = 0.5\%$$

The estimated error of 0.5% was compared with 0.2% and 0.3% found in the experiment.

It was obvious that the concentration obtained from Si is better and quicker than from λ.

Error analysis of method II

From Eq. (1) we obtain

$$\frac{\Delta\lambda}{\Delta Si} = |-155.714 + 3.124 \cdot 2 \cdot Si|$$

The value of Si is about 20 (Table 1) and ΔSi=0.01, then

$$\Delta\lambda = |-155.714 + 3.124 \cdot 2 \cdot 20| \cdot 0.01 = 0.3$$

From Eq. (2)

$$\frac{\Delta\lambda}{\Delta x} = |124.11 - 996.2{\cdot}2x + 3251{\cdot}x^2 - 4315{\cdot}4x^3 + 2250{\cdot}5x^4|$$

when x=0.4, $\Delta\lambda$=0.3

$$\Delta x = \frac{0.3}{71.01} = 0.004$$

then

$$\frac{\Delta x}{x} = \frac{0.004}{0.4} = 1\%$$

The estimated error of 1% is in accord with the experimental data of 0.7% and 0.8% given in Table 2.

Conclusions

The method developed for the determination of the molar concentration of water in binary mixtures of glycerine and water by using Eq. (3) or Eqs (1) and (2) is satisfactory in respect of accuracy and relative error.

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