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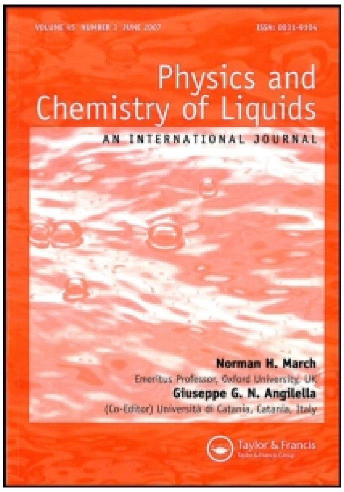

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# Spectroscopic and acoustic study in binary mixtures of glycerol with several alkanols

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Speeds of sound and densities of glycerol + methanol, glycerol + ethanol and glycerol + 2-propanol, were measured over the entire composition range at 298.15 K. The excess volumes, the isentropic compressibilities, molar isentropic compressibilities and excess molar isentropic compressibilities and excess speeds of sound were estimated from the densities and speeds of sound. The results indicated the presence of interactions between unlike molecules through intermolecular hydrogen bonding. The excess volumes, excess molar isentropic compressibilities and excess speeds of sound of the binary mixtures were fitted to the Redlich–Kister equation. The infrared spectra of glycerol + methanol, glycerol + ethanol and glycerol + 2-propanol have been recorded for various concentrations at room temperature. IR stretching frequencies, bandwidths and relative intensities have been estimated and analysed. Acoustic and spectroscopic measurements showed a good correlation to explain the existence of interactions between unlike molecules through intermolecular hydrogen bonding.

**Keywords:** binary mixture; isentropic compressibilities; speed of sound; spectroscopic properties

## 1. Introduction

The molecular interaction and association properties of liquid mixtures have been comprehensively studied by using both acoustic and spectroscopic properties [1–18]. However, there is no systematic study of both acoustic and spectroscopic properties on the behaviour of glycerol with several alkanols.

In this study, the measurements of densities and speeds of sound for glycerol + ethanol, glycerol + 2-propanol and glycerol + methanol mixtures have been made at 298.15 K and under atmospheric pressure. The experimental data was used to obtain isentropic compressibility, $\kappa_s$, molar excess isentropic compressibility, $K_S$, excess molar isentropic compressibility, $K_S^E$ and excess speed of sound, $u^E$ values. The excess molar isentropic compressibility, $K_S^E$, and excess speed of sound, $u^E$, values are used in explaining the molecular interactions in the liquid mixtures. The data for the binary systems were fitted to the Redlich–Kister Equation (1). The infrared (IR) spectra for these systems have also been recorded at room temperature.

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## 2. Experimental

Glycerol ($>99$ mass%), methanol ($>99.8$ mass%), ethanol ($>99.5$ mass%) and 2-propanol ($>99$ mass%) were obtained from Merck. These compounds were used as received without further purification. The mixtures in this study were prepared gravimetrically using an electronic balance (Scaltec, SBC22) accurate to 0.01 mg. The precision of the mole fraction was estimated to be better than $\pm 1 \times 10^{-4}$. The densities and speeds of sound of both pure liquids and liquid mixtures were measured using a vibrating tube densimeter and sound analyser, Anton Paar DSA-5000, automatically thermostated at $\pm 0.01$ K. The calibration of the apparatus was carried out with air and deionised double-distilled water. Precision of the instrument is reported to be $3 \times 10^{-6}\,\mathrm{g\,cm^{-3}}$ for density and $0.1\,\mathrm{ms^{-1}}$ for speeds of sound. The IR spectra for glycerol + methanol, ethanol and 2-propanol were obtained by using a Bruker FT-IR spectrophotometer (Model Tensor 27) at room temperature.

## 3. Results and discussion

### 3.1. *Acoustic analysis of the mixtures*

The experimental values of the density, $\rho$, speeds of sound, $u$, the calculated values for isentropic compressibilities, $\kappa_s$, molar isentropic compressibilities $K_S$, excess molar volume, $V^E$, excess molar isentropic compressibilities, $K_S^E$ and excess speeds of sound, $u^E$, for glycerol + ethanol, glycerol + 2-propanol and glycerol + methanol at 298.15 K and atmospheric pressure are listed in Table 1.

The $\kappa_S$ and $K_S$ were calculated from the following equations:

$$\kappa_S = \frac{1}{\rho u^2}, \tag{1}$$

$$K_S = -\left(\frac{\partial V}{\partial p}\right)_S = V \cdot \kappa_S = \sum_{i=1}^{2} x_i M_i / \left(\rho \cdot u^2\right), \tag{2}$$

where $\rho$ is the density, $V$ is the molar volume, $x_i$ and $M_i$ are the mole fraction and molar mass of component $i$ in the mixture, respectively.

The excess molar volume, $V^E$, is calculated using the expression

$$V^E = \sum_{i=1}^{N} x_i M_i \left(\rho^{-1} - \rho_i^{-1}\right), \tag{3}$$

where $\rho$ is the density of the mixture, $\rho_i$ is the density of pure component $i$, $M_i$ is the molar mass of component $i$, $x_i$ is the mole fraction of component $i$ and $N$ is the number of components.

The excess molar isentropic compressibilities, $K_S^E$, were estimated by means of the equation:

$$K_S^E = K_S - K_S^{id}, \tag{4}$$

where the molar isentropic compressibilities for the ideal mixture, $K_S^{id}$, were calculated by the following relation [3,5]:

$$K_S^{id} = \sum_i x_i \left[K_{S,i}^* - T \cdot A_{p,i}^* \left\{ \left( \sum x_i \cdot A_{p,i}^* \Big/ \sum x_i \cdot C_{p,i}^* \right) - \left( A_{p,i}^* / C_{p,i}^* \right) \right\} \right]. \tag{5}$$

Table 1. Experimental densities, $\rho$, and speeds of sound, $u$, and calculated $K_S$, $K_S^E$, and $u^E$ for glycerol + ethanol, + 2-propanol and + methanol binary mixtures at 298.15 K.

| $x_1$ | $\rho$ (kg m$^{-3}$) | $u$ (m s$^{-1}$) | $K_S$ (m$^3$ PPa$^{-1}$ mol$^{-1}$) | $V^E$ (cm$^3$ mol$^{-1}$) | $K_S^E$ (m$^3$ PPa$^{-1}$ mol$^{-1}$) | $u^E$ (m s$^{-1}$) |
|---|---|---|---|---|---|---|
| Glycerol + methanol | | | | | | |
| 0.0484 | 834.6 | 1163.9 | 37.034 | −0.375 | −4.041 | 48.8 |
| 0.0971 | 876.9 | 1218.1 | 33.196 | −0.646 | −6.692 | 90.3 |
| 0.1808 | 941.4 | 1307.3 | 28.322 | −0.993 | −9.492 | 151.3 |
| 0.2724 | 999.7 | 1397.1 | 24.810 | −1.132 | −10.690 | 201.9 |
| 0.3890 | 1062 | 1504 | 21.718 | −1.178 | −10.779 | 246.8 |
| 0.4994 | 1111.5 | 1598 | 19.662 | −1.134 | −9.937 | 269.2 |
| 0.6081 | 1152.4 | 1680.1 | 18.290 | −0.991 | −8.409 | 266.5 |
| 0.6929 | 1179.5 | 1738.1 | 17.523 | −0.804 | −6.886 | 246.5 |
| 0.8076 | 1211.5 | 1807.9 | 16.786 | −0.505 | −4.490 | 189.8 |
| 0.8967 | 1233.6 | 1860.2 | 16.314 | −0.262 | −2.501 | 121.9 |
| Glycerol + ethanol | | | | | | |
| 0.0434 | 831.1 | 1222.6 | 46.561 | −0.158 | −1.844 | 20.3 |
| 0.0911 | 860.1 | 1251.6 | 43.374 | −0.318 | −3.515 | 41.4 |
| 0.2017 | 921.8 | 1318.7 | 37.459 | −0.473 | −5.874 | 83.1 |
| 0.2993 | 975.4 | 1386.47 | 32.723 | −0.725 | −7.422 | 120.1 |
| 0.4068 | 1027.8 | 1463.5 | 28.639 | −0.755 | −7.942 | 153.3 |
| 0.4994 | 1071.1 | 1536.9 | 25.485 | −0.801 | −7.982 | 179.3 |
| 0.5992 | 1114.4 | 1618 | 22.656 | −0.776 | −7.410 | 197.2 |
| 0.6989 | 1153.3 | 1697.1 | 20.427 | −0.616 | −6.194 | 197.3 |
| 0.7974 | 1190.2 | 1775.6 | 18.535 | −0.481 | −4.637 | 176.8 |
| 0.8959 | 1224.1 | 1844.9 | 17.117 | −0.274 | −2.562 | 117.7 |
| Glycerol + 2-propanol | | | | | | |
| 0.0647 | 812.7 | 1173.4 | 68.368 | −0.196 | −3.483 | 25.9 |
| 0.1159 | 837.4 | 1198.3 | 63.368 | −0.309 | −5.506 | 44.3 |
| 0.2100 | 884.6 | 1247.2 | 54.895 | −0.625 | −8.488 | 77.0 |
| 0.2911 | 924.4 | 1291.5 | 48.703 | −0.768 | −9.925 | 102.4 |
| 0.3850 | 970.2 | 1349.1 | 42.269 | −0.877 | −10.828 | 131.3 |
| 0.4922 | 1021.7 | 1425.9 | 35.739 | −0.888 | −11.003 | 164.3 |
| 0.6061 | 1075.4 | 1520.3 | 29.738 | −0.786 | −10.202 | 194.6 |
| 0.7027 | 1122.2 | 1617.3 | 25.072 | −0.757 | −9.056 | 216.9 |
| 0.8066 | 1171.1 | 1728.3 | 20.974 | −0.612 | −6.852 | 215.6 |
| 0.9073 | 1216.5 | 1829.9 | 17.988 | −0.326 | −3.675 | 155.2 |

$A^*_{p,i}$, $C^*_{p,i}$ and $K^*_{S,i}$ are the product of the molar volume $V_i$ and the isobaric expansivity $\alpha^*_{p,i}$, isobaric molar heat capacity of the pure component $i$ and the product of the molar volume $V_i$ and the isentropic compressibility $\kappa^*_{S,i}$, referred to pure liquid component $i$, respectively.

The excess speed of sound, $u^E$, of each sample with respect to ideal behaviour is defined by the equation:

$$u^E = u - u^{id} = u - \left(\rho^{id}\kappa_S^{id}\right)^{-1/2}, \tag{6}$$

where $u$ is the speed of sound of the mixture, $\rho^{id} = \sum_{i=1}\phi_i\rho_i$ is the density of the corresponding ideal mixture [4], and $\rho_i$ is the density of pure component $i$. $\phi_i$ is defined by the relation:

$$\phi_i = \frac{x_i V_i}{\left(\sum_i x_i V_i\right)}, \tag{7}$$

Table 2. Values of the parameters $A_i$ of the Redlich–Kister equation and corresponding standard deviations, $\sigma$, at 298.15 K.

| | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma$ |
|---|---|---|---|---|---|
| Glycerol + methanol | | | | | |
| $V^E$ (cm$^3$ mol$^{-1}$) | −4.511 | 1.952 | −0.935 | 1.587 | 0.0113 |
| $u^E$ (m s$^{-1}$) | 1072.0 | 176.4 | 143.7 | −12.3 | 1.04 |
| $K_S^E$ (m$^3$ PPa$^{-1}$ mol$^{-1}$) | −39.323 | 21.824 | −17.930 | 14.786 | 0.0824 |
| Glycerol + ethanol | | | | | |
| $V^E$ (cm$^3$ mol$^{-1}$) | −3.176 | 0.157 | 0.096 | 0.387 | 0.0313 |
| $u^E$ (m s$^{-1}$) | 715.8 | 465.6 | 258.7 | 29.9 | 0.81 |
| $K_S^E$ (m$^3$ PPa$^{-1}$ mol$^{-1}$) | −31.787 | 5.747 | −3.544 | 4.655 | 0.0747 |
| Glycerol + 2-propanol | | | | | |
| $V^E$ (cm$^3$ mol$^{-1}$) | −3.549 | 0.590 | −0.326 | −1.889 | 0.0261 |
| $u^E$ (m s$^{-1}$) | 657.5 | 594.5 | 706.3 | 413.4 | 1.18 |
| $K_S^E$ (m$^3$ PPa$^{-1}$ mol$^{-1}$) | −43.911 | 5.746 | −9.439 | 1.604 | 0.0630 |

The excess molar isentropic compressibilities, $K_S^E$ and excess speeds of sound, $u^E$ of the binary mixtures were fitted with a Redlich–Kister equation [19]:

$$\Delta Q = x(1-x)\sum_{k=0}^{m} A_k(2x-1)^k, \tag{8}$$

where $\Delta Q$ is $V^E$, $K_S^E$ or $u^E$, $x_i$ is the mole faction of component $i$, $A_k$ is the polynomial coefficient, $k$ is the number of the polynomial coefficients and $m$ is the number of parameters. The coefficients $A_k$ of Equation (8) are presented in Table 2.

The standard deviations were calculated using the expression,

$$\sigma = \left[\frac{\sum_i^N \left(Z_{\text{exp}} - Z_{\text{pred}}\right)^2}{N-1}\right]^{1/2}, \tag{9}$$

where $Z$ is the value of the property and $N$ is the number of experimental data.

The values of the excess molar volume, $V^E$, the excess molar isentropic compressibilities, $K_S^E$ and excess speed of sound, $u^E$, plotted against the mole fraction of glycerol of the binary liquid mixtures in each case, are given in Figures 1, 2 and 3, respectively.

The excess molar volume, $V^E$, the excess isentropic compressibilities, $K_S^E$, were negative over the entire composition for all studied binary mixtures. The excess speed of sound, $u^E$ were positive over the whole composition range for all the binary mixtures. For all binary liquid mixtures, $V^E$ and $K_S^E$ curves showed similar behaviours, while the curves of $u^E$ showed an opposite trend (Figures 1–3).

The behaviour of a studied system can be explained in the terms of molecular interactions. According to the literature [6], the excess molar volume, $V^E$ and the excess isentropic compressibilities, $K_S^E$, decreases and becomes increasingly negative as the strength of the interaction between the components increases, due to a closer approach of unlike molecules leading to reductions in compressibility. The reported excess molar

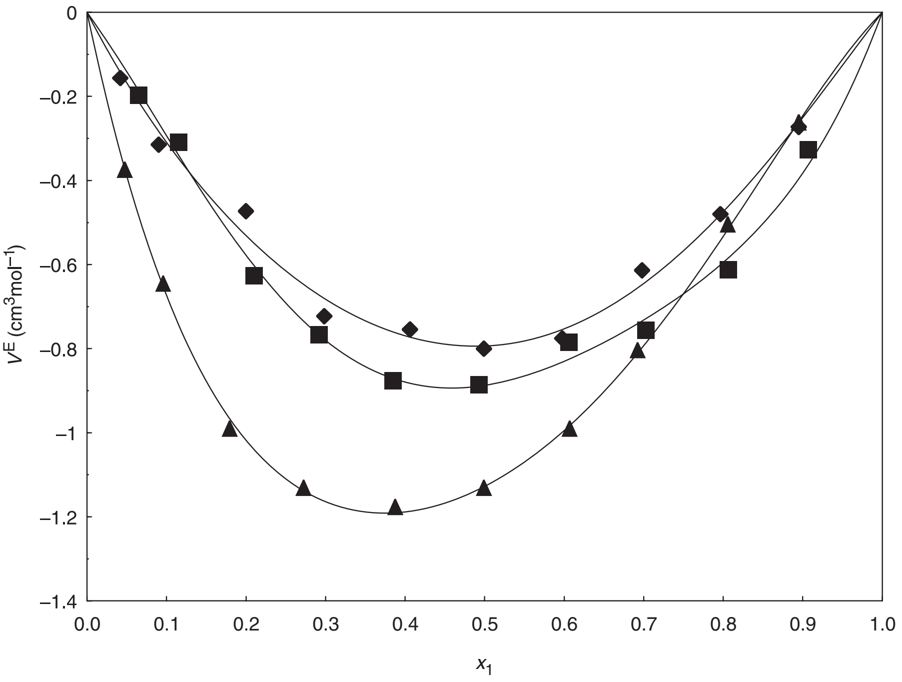

Figure 1. Excess molar volume, $V^E$, for the binary mixtures at 298.15 K: glycerol + 2-propanol (■), glycerol (1) + ethanol (2) (◆), glycerol (1) + methanol (2) (▲) and Redlich–Kister's correlation (—).

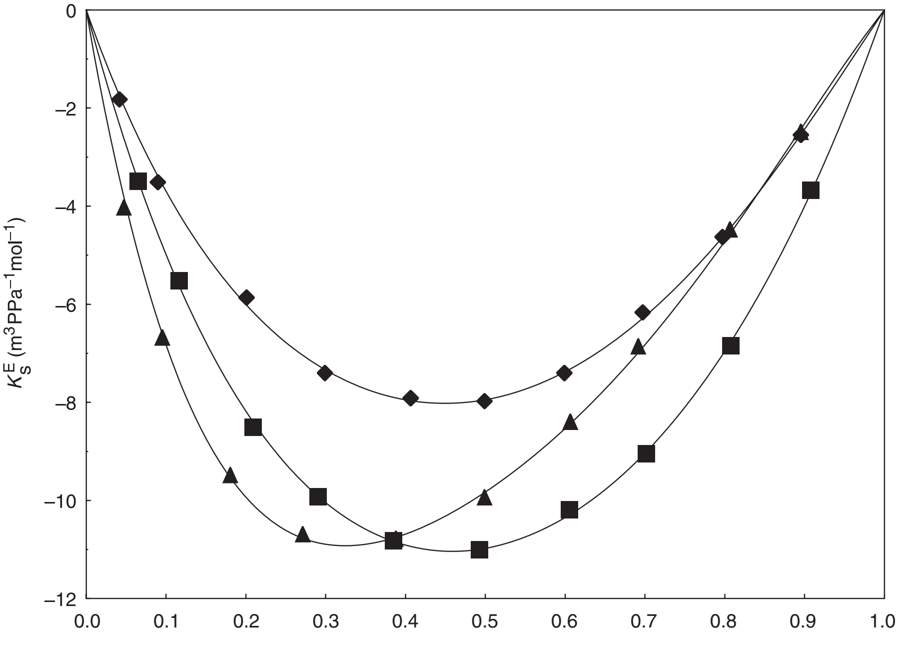

Figure 2. Excess isentropic compressibilities, $K_S^E$, for the binary mixtures at 298.15 K: glycerol + 2-propanol (■), glycerol (1) + ethanol (2) (◆), glycerol (1) + methanol (2) (▲) and Redlich–Kister's correlation (—).

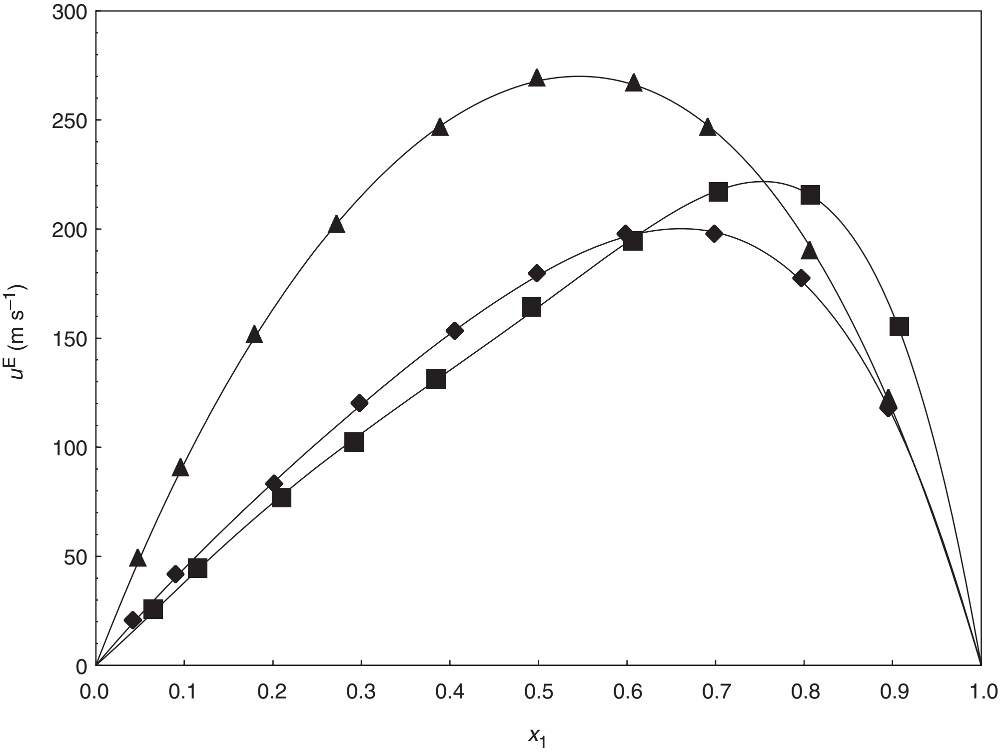

Figure 3. Excess speed of sound, $u^E$ for the binary mixtures at 298.15 K: glycerol + 2-propanol (■), glycerol (1) + ethanol (2) (◆), glycerol (1) + methanol (2) (▲) and Redlich–Kister's correlation (—).

volume, $V^E$, excess isentropic compressibilities, $K_S^E$ and excess speed of sound, $u^E$ values may be explained in terms of:

(a) The self-associations of molecules, (b) Steric hindrance due to branching of the secondary alkanol, 2-propanol and (c) The intermolecular associations between unlike molecules.

The first two effects are supposed to cause the positive contribution to $V^E$ and $K_S^E$ and negative contribution to $u^E$. The third one causes more negative values of $V^E$ and $K_S^E$ but supplies a positive contribution to $u^E$.

### 3.2. *IR spectra of the mixtures*

Infrared spectra of these binary mixtures which were prepared with these three alkanols, i.e. methanol, ethanol, 2-propanol and glycerol showed strong hydrogen bonding capability as expected. As it is known, hydrogen bonding broadens and raises the maximum of free O–H bands to longer wavelength [20].

In this study, none of the investigated systems showed free –OH band and the existence of intermolecular hydrogen bonding between both like and unlike molecules lowered the O–H stretching frequency and raised the bandwidths. In the glycerol + methanol mixtures, the maximum decrease in frequency, the highest relative intensity and the maximal band broadening were observed at the equimolar glycerol + methanol mixture (Figure 4). Glycerol + methanol mixtures showed the highest level of association arised from the

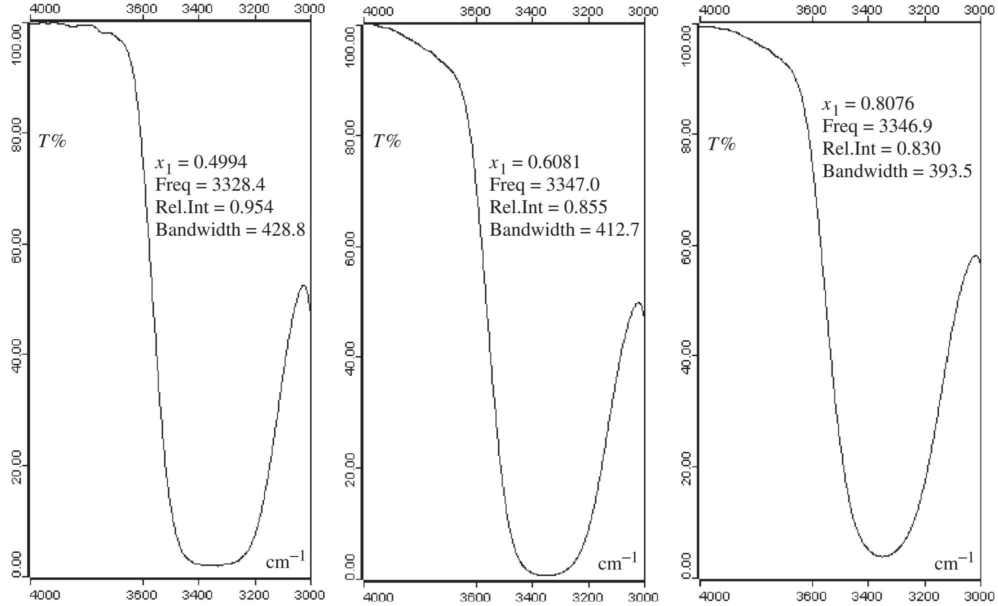

Figure 4. Observed O–H stretching bands in the IR spectra of glycerol + methanol at various concentrations.

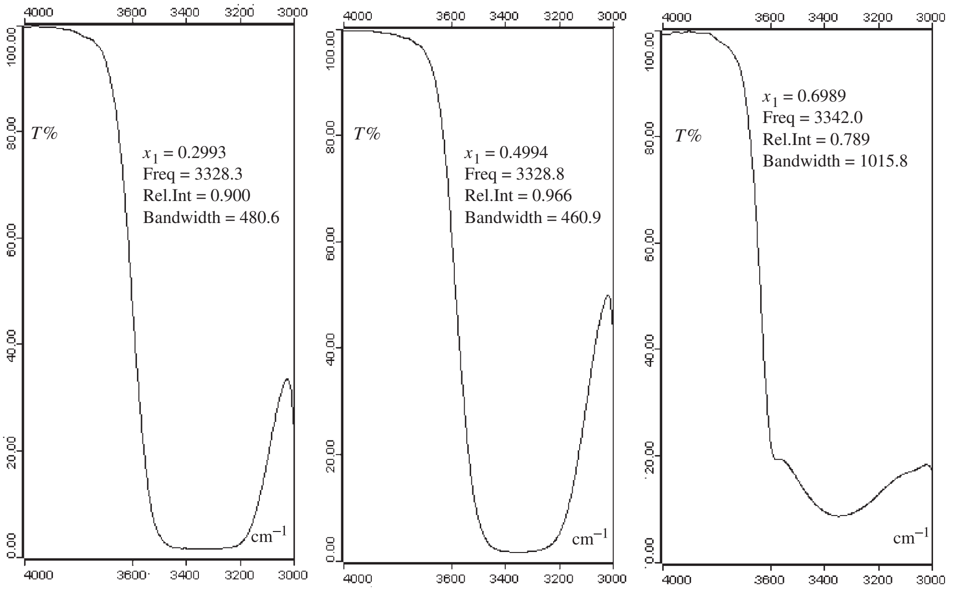

Figure 5. O–H stretching bands in the IR spectra of glycerol + ethanol at various concentrations.

hydrogen bonding interaction between unlike molecules at this mole fraction. It is seen in Table 1 that the highest deviation in the excess speed of sound was also observed at this concentration. In the mixtures with the glycerol content more than 0.5, mole fraction showed some increase in the stretching frequencies, but a decrease in bandwidth and

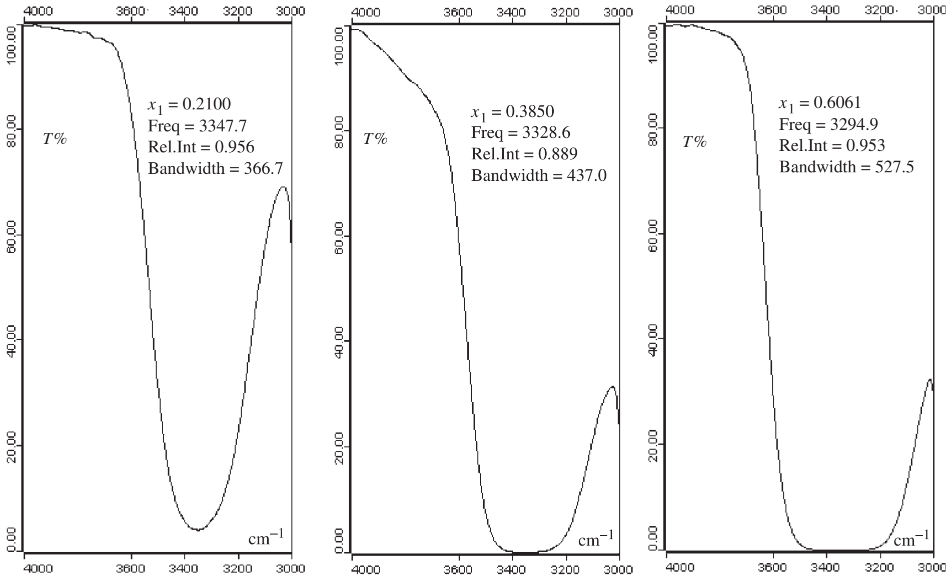

Figure 6. O–H stretching bands in the IR spectra of glycerol + 2-propanol at various concentrations.

relative intensities (Figure 4). The more the glycerol contents in the mixtures increase, the more possibility of self-association of triol molecules appears and it is known that self-association and cross H-bonds are strong enough to compact the mixtures and as it was mentioned above, decrease in negative values of $V^E$ and $K_S^E$ and decrease in positive values of $u^E$ must be raised from this fact.

In the glycerol + ethanol mixtures, the highest deviation in the excess speed of sound appeared at the mixtures of 0.7 glycerol mole fraction and its IR spectrum showed a very broad band. At this concentration in which the value of the relative intensity was also very high, the intermolecular association between unlike molecules must be at the highest level (Figure 5). The decrease of stretching frequency were less than the ethanol-rich ones probably due to the high possibility of self-association between these triol molecules. At higher amounts of ethanol (i.e. at smaller $x_1$ values) the mixtures showed lesser negative $V^E$ and $K_S^E$ values and smaller $u^E$ values, probably because of decreasing in the possibility of hydrogen bonding between unlike molecules.

Infrared spectra of glycerol + 2-propanol mixtures showed that the highest frequency decreases and broadening of bandwidth arising from intermolecular hydrogen bonding were observed at the mixture of 0.6 glycerol mole fraction. As seen in Figure 6, in the 2-propanol-rich mixtures, the frequencies of O–H stretching bands were higher and the bandwidths were less than glycerol-rich ones probably because of the weaker association of 2-propanol due to its steric hindrance, which causes higher values of $V^E$ and $K_S^E$ while values of $u^E$ are lower.

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