Densities, Viscosities and Refractive Indices of Ternary System Cyclohexane + Cyclohexanol + Cyclohexanone at 293.15, 298.15 and 303.15 K

MARIA MAGDALENA BUDEANU*, VASILE DUMITRESCU
Chemistry Department, Petroleum and Gas University of Ploiesti, 39 Bucuresti Blvd., 100520, Ploiesti, Romania

Densities ($\rho$), viscosities ($\eta$) and refractive indices ($n_\lambda$) of the ternary system cyclohexane + cyclohexanol + cyclohexanone were measured at 293.15, 298.15 and 298.15 K and atmospheric pressure, over the whole composition range. The experimental values of densities and viscosities were correlated with temperature using a linear equation and Guzman equation respectively. Viscosity results were fitted with Grunberg-Nissan equation and Heric-Brewer equation. Different refractive index mixing rules (Arago-Biot, Dale-Glastone, Newton and Lorentz-Lorenz) were studied for this ternary system. The functions of activation of viscous flow were also calculated and their variations with compositions have been discussed.

Keywords: ternary mixtures, density, viscosity, refractive index

Thermophysical properties of multi-component liquid mixtures are essential for process designing as well as for understanding structural and packing changes of molecules in mixtures. The design and operation of processes that involve non-electrolyte mixtures require knowledge of rigorous models or experimental data to represent the non-ideality of mixtures [1].

Density, viscosity and refractive index are the physicochemical properties which provide important information, useful for different problems in chemical engineering in order to develop industrial processes, as well as for database applications and model formulations [2]. The correct values of liquid density are important because they are involved in the equations of heat, mass and momentum transfer [3].

Cyclohexane is widely used as a solvent, polar additive, dilution initiator, structure regulator and active additive in the synthesis of copolymer, resins and rubber [4].

Cyclohexanol finds applications as an intermediate substance in the production of nylon and plasticizers. It acts as a stabilizer in soap and detergent making and as a solvent in paint and textile industries [5].

Cyclic and linear alcohols are associated through the hydrogen bond in the pure state as well as in mixtures. The degree of association in alkanols containing cyclic alky1 group is very low due to steric factors [6].

Cyclic ketones are important intermediates in the synthesis of many organic compounds important for the chemical, pharmaceutical, and cosmetic industries [7-9].

Cyclohexanone can be used as raw material in the production of cycloalkanes, caprolactam and the monomers used for the synthesis of Nylon 6 and 66 [10,11].

This paper reports densities, viscosities and refractive indices of ternary mixtures of cyclohexane + cyclohexanol + cyclohexanone as function of composition at 293.15, 298.15 and 303.15 K and atmospheric pressure. A literature survey has shown that the thermophysical properties for the ternary system studied have not been reported.

Experimental part

The chemicals cyclohexane (mole fraction purity > 0.997) was supplied by Merck, cyclohexanol (mole fraction purity > 0.998) and cyclohexanone (mole fraction purity > 0.98) were obtained from Chemical Company. The purity was verified by chromatographic analysis. The mole fractions were determined by weighing with a precision of ± 10^-4 g. The experimental error in mole fraction is estimated to be ± 0.0001.

The densities of the pure components and of the ternary solutions are measuring using a calibrated glass pycnometer having a bulb volume of 10 cm^3. The pycnometer filled with a liquid was kept in a thermostatically bath (maintained constant to ± 0.05 K) for 15 min to achieve thermal equilibrium [12]. The estimated uncertainty for density was ± 0.0003 g cm^-3.

Viscosities were determined with an Ubbelohde kinematic viscometer [13] that was kept in a vertical position in a thermostatically bath (U 10 constant to ± 0.05 K).

The kinetic viscosity was calculated using the relation:

$$\nu = \frac{At - B}{t}$$

where $\nu$ is the kinematic viscosity, $t$ (s) is its flow time in the viscometer, and $A$ and $B$ are characteristic constants of the used viscometer. The constants $A$ and $B$ were determined by using bidistilled water and benzene as the calibrating liquids. Accuracy of time measurement is ± 0.01s.

The dynamic viscosity was determined from the equation:

$$\eta = \nu \rho$$

where $\rho$ is the density of the liquid. The precision of the viscosity to be ± 0.0004 mPa s. The refractive indices of pure liquids and their ternary mixtures were measured using a thermostated Abbe refractometer. Calibration of the instruments was done by measuring the refractive indices of double-distilled water and toluene at known temperature. The values of refractive index were obtained using sodium D light.

The temperature of the test liquids between the prism and the prism jacket during the measurements was maintained to an accuracy of ±0.05 K by circulating water through the jacket around the prism from a controlled thermostatic bath and the temperature was measured with an digital thermometer connected with the prism jacket.

* email: maria.budeanu@upg-ploiesti.ro
Results and discussions

The measured densities, viscosities and refractive indices of the pure components are presented in table 1.

Cyclohexane densities values reported in the literature differ from our values with a maximum 0.1%. For cyclohexanol, densities values published in the literature differ from our experimental data with a maximum 0.11% and for cyclohexanone values differ with maximum 0.04%. Viscosity values reported in the literature differ from our data with a maximum 0.95% for cyclohexane, with maximum 2.8% for cyclohexanol and for cyclohexanone with maximum 1.2%.

The differences between measured and literature data of refractive indices are less than 0.02% for cyclohexane, less than 0.01% for cyclohexanol and maximum 0.05% for cyclohexanone. The densities, viscosities and refractive indices of the ternary mixtures of cyclohexane + cyclohexanol + cyclohexanone are reported in tables 2-4.

### Table 1

| Component        | \( T \) / K | \( \rho \) / g cm\(^{-3}\) | \( \eta \) / mPa s | \( n_\lambda \)   |
|------------------|-------------|-----------------|------------------|------------------|
| Cyclohexane      | 293.15      | 0.7771          | -                | 0.9689           |
|                  | 298.15      | 0.7731          | -                | 0.9037[15]       |
|                  | 303.15      | 0.7693          | -                | 0.8212[15]       |
| Cyclohexanol     | 293.15      | 0.9498          | -                | 61.1025          |
|                  | 298.15      | 0.9401          | -                | 50.7049[17]      |
|                  | 303.15      | 0.9420          | -                | 39.3835          |
| Cyclohexanone    | 293.15      | 0.9483          | -                | 2.0306           |
|                  | 298.15      | 0.9439[1]       | -                | 2.1068[8]        |
|                  | 303.15      | 0.9399          | -                | 1.9030           |

### Table 2

| \( x_1 \) | \( x_2 \) | Density / g cm\(^{-3}\) | Temperature / K |
|-----------|-----------|--------------------------|-----------------|
| 0.0591    | 0.1023    | 0.9291                   | 293.15 - 298.15 |
| 0.1462    | 0.1740    | 0.9221                   | 0.9221          |
| 0.1957    | 0.2005    | 0.9138                   | 0.9138          |
| 0.2161    | 0.2200    | 0.9096                   | 0.9096          |
| 0.2396    | 0.3049    | 0.8934                   | 0.8934          |
| 0.2993    | 0.3973    | 0.8796                   | 0.8796          |
| 0.4484    | 0.4574    | 0.8700                   | 0.8700          |
| 0.1079    | 0.7688    | 0.9295                   | 0.9295          |
| 0.1201    | 0.8936    | 0.9231                   | 0.9231          |
| 0.1994    | 0.5982    | 0.9141                   | 0.9141          |
| 0.2514    | 0.4950    | 0.8994                   | 0.8994          |
| 0.2982    | 0.4027    | 0.8908                   | 0.8908          |
| 0.3034    | 0.1950    | 0.8780                   | 0.8780          |
| 0.4453    | 0.1039    | 0.8703                   | 0.8703          |
| 0.8128    | 0.0922    | 0.8092                   | 0.8092          |
| 0.3582    | 0.2030    | 0.8468                   | 0.8468          |
| 0.6004    | 0.2018    | 0.8446                   | 0.8446          |
| 0.4885    | 0.2535    | 0.8512                   | 0.8512          |
| 0.3999    | 0.2965    | 0.8732                   | 0.8732          |
| 0.1956    | 0.4168    | 0.9111                   | 0.9111          |
| 0.1002    | 0.4509    | 0.9304                   | 0.9304          |

### Table 3

| \( x_1 \) | \( x_2 \) | Viscosity / mPa s | Temperature / K |
|-----------|-----------|-------------------|-----------------|
| 0.0581    | 0.1053    | 2.3956             | 2.5553          |
| 0.1462    | 0.1740    | 2.5976             | 2.5857          |
| 0.1957    | 0.2005    | 2.5499             | 2.5317          |
| 0.2161    | 0.2200    | 2.5978             | 2.5332          |
| 0.2396    | 0.3049    | 2.3952             | 2.3532          |
| 0.2993    | 0.3973    | 3.5716             | 3.0632          |
| 0.4484    | 0.4774    | 4.1056             | 3.5153          |
| 0.1079    | 0.7688    | 17.8073            | 13.8180         |
| 0.1201    | 0.8936    | 11.5411            | 9.3446          |
| 0.1994    | 0.5982    | 7.6866             | 6.6811          |
| 0.2514    | 0.4950    | 5.1674             | 4.3442          |
| 0.3582    | 0.4027    | 3.8431             | 3.3939          |
| 0.5004    | 0.1930    | 2.2103             | 1.9509          |
| 0.4455    | 0.1039    | 1.7404             | 1.6233          |
| 0.8128    | 0.0922    | 1.2732             | 1.1977          |
| 0.5852    | 0.2030    | 1.8910             | 1.7508          |
| 0.6004    | 0.2018    | 1.8776             | 1.7033          |
| 0.4985    | 0.2353    | 2.3603             | 2.0139          |
| 0.3599    | 0.2965    | 2.8013             | 2.4098          |
| 0.1658    | 0.4168    | 4.4200             | 3.7218          |
| 0.1002    | 0.4509    | 4.8115             | 4.1473          |
Densities of the pure components and ternary mixtures were correlated with temperature using the relation \[ \rho = \rho_o + \alpha_1 T \] 

Viscosities of the pure compounds and ternary solutions were correlated with temperature using the equation \[ \eta = \eta_0 e^{\varepsilon/\eta} \] 

where \( \eta_0 \) and \( \varepsilon/\eta \) are the adjustable parameters.

The adjustable parameters of these equations were estimated using the experimental data and a nonlinear regression analysis employing the Levenberg-Marquardt algorithm [23]. Tables 5 and 6 show the fitting parameters along with the correlation square coefficient \( r^2 \) and standard deviation \( \sigma \) calculated with equation:

\[ \sigma = \left[ \frac{\sum(X_{\text{exp}} - X_{\text{calc}})^2}{m-n} \right]^{1/2} \]

The values of the standard deviation \( \sigma \) and the correlation square coefficient \( r^2 \) indicate that the equations tested are able to correlate good the experimental values of the densities and viscosities.

**Viscosity data modeling**

The viscosity correlation equations used for binary mixtures have been extended to ternary systems by introducing ternary adjustable parameters. The correlating ability of the Grunberg-Nissan equations with three binary parameters and respectively four parameters (three binary and one ternary) and also of the Heric-Brewer equation was tested in this work.

---

| \( x_1 \) | \( x_2 \) | \( x_3 \) | Refractive index | Temperature / K |
|---|---|---|---|---|
| 0.0981 | 0.1053 | 0.1053 | 1.4315 | 295.13 |
| 0.1462 | 0.1740 | 0.1740 | 1.4424 | 298.13 |
| 0.1953 | 0.2065 | 0.2065 | 1.4554 | 301.13 |
| 0.2161 | 0.2200 | 0.2200 | 1.4400 | 295.13 |
| 0.2386 | 0.3049 | 0.3049 | 1.4486 | 298.13 |
| 0.2993 | 0.3973 | 0.3973 | 1.4480 | 301.13 |
| 0.4484 | 0.4574 | 0.4574 | 1.4458 | 295.13 |
| 0.179 | 0.7868 | 0.7868 | 1.4359 | 298.13 |
| 0.1501 | 0.6926 | 0.6926 | 1.4455 | 301.13 |
| 0.1594 | 0.5982 | 0.5982 | 1.4451 | 295.13 |
| 0.2514 | 0.4950 | 0.4950 | 1.4333 | 298.13 |
| 0.2982 | 0.4017 | 0.4017 | 1.4486 | 301.13 |
| 0.3904 | 0.1930 | 0.1930 | 1.4460 | 295.13 |
| 0.4455 | 0.1039 | 0.1039 | 1.4406 | 298.13 |
| 0.8128 | 0.0922 | 0.0922 | 1.4347 | 301.13 |
| 0.5852 | 0.2830 | 0.2830 | 1.4400 | 295.13 |
| 0.6004 | 0.2018 | 0.2018 | 1.4394 | 298.13 |
| 0.4905 | 0.2535 | 0.2535 | 1.4427 | 301.13 |
| 0.3999 | 0.2865 | 0.2865 | 1.4456 | 295.13 |
| 0.1956 | 0.4168 | 0.4168 | 1.4332 | 298.13 |
| 0.1002 | 0.4509 | 0.4509 | 1.4348 | 301.13 |

Table 4

**EXPERIMENTAL VALUES FOR REFRACTIVE INDICES \( n_D \) OF THE CYCLOHEXANE \( x_1 \) + CYCLOHEXANOL \( x_2 \) + CYCLOHEXANONE SYSTEM**

---

| \( x_1 \) | \( x_2 \) | \( x_3 \) | Densities of the pure compounds and ternary solutions were correlated with temperature using the relation \[ \rho = \rho_o + \alpha_1 T \] 
Viscosities of the pure compounds and ternary solutions were correlated with temperature using the equation \[ \eta = \eta_0 e^{\varepsilon/\eta} \] 
where \( \eta_0 \) and \( \varepsilon/\eta \) are the adjustable parameters.

The adjustable parameters of these equations were estimated using the experimental data and a nonlinear regression analysis employing the Levenberg-Marquardt algorithm [23]. Tables 5 and 6 show the fitting parameters along with the correlation square coefficient \( r^2 \) and standard deviation \( \sigma \) calculated with equation:

\[ \sigma = \left[ \frac{\sum(X_{\text{exp}} - X_{\text{calc}})^2}{m-n} \right]^{1/2} \]

The values of the standard deviation \( \sigma \) and the correlation square coefficient \( r^2 \) indicate that the equations tested are able to correlate good the experimental values of the densities and viscosities.

**Viscosity data modeling**

The viscosity correlation equations used for binary mixtures have been extended to ternary systems by introducing ternary adjustable parameters. The correlating ability of the Grunberg-Nissan equations with three binary parameters and respectively four parameters (three binary and one ternary) and also of the Heric-Brewer equation was tested in this work.

---

| \( x_1 \) | \( x_2 \) | \( x_3 \) | 10^6 \( \alpha_0 \) | 10^6 \( \alpha_1 \) | 10^6 \( \sigma \) / g cm^2 | \( r^2 \) |
|---|---|---|---|---|---|---|
| 1 | 0 | 1.1785 | -7.8 | 1.63 | 0.992 | 0.993 |
| 0 | 1 | 1.1339 | -6.4 | 0.00 | 1.000 | 0.996 |
| 0.0981 | 0.1053 | 1.1021 | -5.9 | 2.04 | 0.985 | 0.990 |
| 0.1462 | 0.1740 | 1.1624 | -8.2 | 1.63 | 0.994 | 0.990 |
| 0.1953 | 0.2065 | 1.2038 | -9.9 | 6.12 | 0.984 | 0.990 |
| 0.2161 | 0.2200 | 1.1731 | -9.0 | 6.53 | 0.979 | 0.990 |
| 0.2993 | 0.3049 | 1.1453 | -8.6 | 4.90 | 0.987 | 0.990 |
| 0.3999 | 0.3973 | 1.1491 | -9.2 | 4.90 | 0.987 | 0.990 |
| 0.4484 | 0.4574 | 1.1612 | -8.4 | 0.82 | 0.996 | 0.990 |
| 0.5852 | 0.5982 | 1.1748 | -8.0 | 4.49 | 0.939 | 0.990 |
| 0.1501 | 0.6926 | 1.2012 | -9.5 | 5.30 | 0.987 | 0.990 |
| 0.2514 | 0.3049 | 1.1097 | -8.8 | 0.82 | 0.994 | 0.990 |
| 0.3999 | 0.4027 | 1.1438 | -8.7 | 1.22 | 0.999 | 0.990 |
| 0.4905 | 0.1930 | 1.1123 | -8.5 | 3.26 | 0.994 | 0.990 |
| 0.4455 | 0.1039 | 1.1179 | -10.3 | 6.12 | 0.980 | 0.990 |
| 0.8128 | 0.0922 | 1.1283 | -10.9 | 8.57 | 0.976 | 0.990 |
| 0.3852 | 0.3050 | 1.1868 | -11.6 | 1.63 | 0.992 | 0.990 |
| 0.8604 | 0.2018 | 1.1373 | -10.0 | 4.90 | 0.990 | 0.990 |
| 0.4905 | 0.2135 | 1.1248 | -9.0 | 5.71 | 0.984 | 0.990 |
| 0.1956 | 0.4168 | 1.1280 | -7.4 | 0.82 | 0.996 | 0.990 |
| 0.1002 | 0.4509 | 1.2020 | -9.3 | 2.86 | 0.962 | 0.990 |

Table 5

**PARAMETERS FOR DENSITY DATA, STANDARD DEVIATION AND CORRELATION SQUARE COEFFICIENT FOR CYCLOHEXANE \( x_1 \) - CYCLOHEXANOL \( x_2 \) - CYCLOHEXANONE**
Table 6
PARAMETERS FOR VISCOSITY DATA, STANDARD DEVIATION AND CORRELATION SQUARE COEFFICIENT FOR CYCLOHEXANE (x₁) - CYCLOHEXANOL (x₂) - CYCLOHEXANONE

| x₁  | x₂  | 10^4 η₀ | Eₗ / kJ mol⁻¹ | σ / mPa s | r²  |
|-----|-----|--------|--------------|----------|-----|
| 0   | 0   | 54.9   | 12.6         | 0.003    | 0.9853 |
| 0   | 1   | 2.05   | 30.7         | 1.517    | 0.9795 |
| 0.0981 | 0.1023 | 65.9 | 14.1         | 0.003    | 0.9993 |
| 0.1462 | 0.1740 | 66.3 | 15.1         | 0.004    | 0.9996 |
| 0.1957 | 0.2005 | 11.7 | 18.8         | 0.021    | 0.9945 |
| 0.2151 | 0.2200 | 22.6 | 17.2         | 0.020    | 0.9949 |
| 0.2986 | 0.3049 | 47.7 | 15.6         | 0.024    | 0.9926 |
| 0.3993 | 0.3973 | 4.16 | 22.1         | 0.005    | 0.9999 |
| 0.4484 | 0.4574 | 2.46 | 23.7         | 0.024    | 0.9981 |
| 0.1079 | 0.7868 | 0.083 | 35.4         | 0.129    | 0.9985 |
| 0.1501 | 0.6956 | 0.43 | 30.5         | 0.013    | 0.9999 |
| 0.1994 | 0.5882 | 1.36 | 26.0         | 0.002    | 0.9939 |
| 0.2514 | 0.6653 | 4.32 | 22.9         | 0.061    | 0.9821 |
| 0.2882 | 0.4027 | 5.52 | 21.3         | 0.017    | 0.9987 |
| 0.3904 | 0.1959 | 12.3 | 17.7         | 0.003    | 0.9996 |
| 0.4455 | 0.1039 | 88.1 | 12.9         | 0.027    | 0.9646 |
| 0.8128 | 0.0922 | 72.6 | 12.6         | 0.026    | 0.9543 |
| 0.3852 | 0.2030 | 35.3 | 15.2         | 0.028    | 0.9679 |
| 0.6004 | 0.2018 | 65.7 | 13.8         | 0.004    | 0.9994 |
| 0.4965 | 0.2533 | 6.39 | 20.0         | 0.037    | 0.9827 |
| 0.3999 | 0.2965 | 8.74 | 19.7         | 0.033    | 0.9856 |
| 0.1956 | 0.4168 | 7.43 | 21.1         | 0.009    | 0.9729 |
| 0.1002 | 0.4509 | 6.41 | 21.7         | 0.004    | 0.9999 |

The Grunberg-Nissan equation [24] with three binary parameters is:

$$\eta = x_1 \eta_1 + x_2 \eta_2 + x_3 \eta_3 + x_1 x_2 d_{12} + x_1 x_3 d_{13} + x_2 x_3 d_{23}$$  \( (6) \)

The Grunberg-Nissan equation [24] with four parameters is:

$$\eta = x_1 \eta_1 + x_2 \eta_2 + x_3 \eta_3 + x_1 x_2 d_{12} + x_1 x_3 d_{13} + x_2 x_3 d_{23} + x_1 x_2 x_3 d_{123}$$  \( (7) \)

The Heric-Brewer equation [25] for ternary system is:

$$\eta = x_1 \eta_1 + x_2 \eta_2 + x_3 \eta_3 + x_1 x_2 M_1 + x_1 x_3 M_2 + x_2 x_3 M_3$$

$$-\ln(x_1 M_1 + x_2 M_2 + x_3 M_3) + x_1 x_2 [\alpha_{12} + \alpha_{21}(x_1 - x_2)]$$

$$+ x_1 x_3 [\alpha_{13} + \alpha_{31}(x_1 - x_2)] + x_2 x_3 [\alpha_{23} + \alpha_{32}(x_2 - x_3)] + x_1 x_2 x_3 \alpha_{123}$$  \( (8) \)

Table 7 shows the parameters calculated and the standard deviations (σ) calculated using the equation 5, where Xexp is the experimental viscosity, Xcalc is the calculated viscosity and n is the number of adjustable parameters. Figure 1 shows experimental and calculated values (equations 6-8) of viscosities at 298.15 K.

As can be seen in figure 1 the values calculated with the Heric-Brewer equation are closer to the bisector of the diagram which shows that this equation can be used with good results for the correlation of viscosity.

| Equation | Parameters and σ (mPa s) | Temperature / K |
|----------|--------------------------|-----------------|
| Grunberg-Nissan with three parameters | | |
| G-N (1)  | d₁₁ 2.1380 ; 2.3512 ; -2.3006 | 293.15 298.15 302.15 |
|          | d₁₂ 0.1967 ; 0.4558 ; 0.4901 | |
|          | d₁₃ -2.6536 ; -2.9466 ; -2.8043 | |
|          | σ 0.029 ; 0.036 ; 0.042 | |
| Grunberg-Nissan with four parameters | | |
| G-N (2)  | d₁₁ 2.2371 ; 2.2375 ; 2.2609 | |
|          | d₁₂ -0.0397 ; 0.2204 ; 0.0029 | |
|          | d₁₃ 2.8463 ; 3.1476 ; 3.1574 | |
|          | d₁₂₃ 2.5617 ; 2.4213 ; 4.2509 | |
|          | σ 0.027 ; 0.035 ; 0.037 | |
| Heric-Brewer (H-B) | | |
|       | a₁₁ 2.1484 ; 2.3325 ; 2.2785 | |
|       | a₁₂ 2.8717 ; 1.5984 ; 2.3572 | |
|       | a₁₃ -0.3400 ; -0.3617 ; -0.4457 | |
|       | a₂₁ 2.5354 ; -0.3915 ; 0.4429 | |
|       | a₂₂ 2.9383 ; -0.9248 ; -2.5443 | |
|       | a₂₃ 3.5486 ; 0.0587 ; 0.6828 | |
|       | a₃₁ 3.2183 ; 2.3528 ; 4.0364 | |
|       | σ 0.020 ; 0.024 ; 0.024 | |
Fig. 1. Calculated viscosity (◊ G-N (1), ◊ G-N (2), Δ H-B) versus experimental viscosity (continuous line) at 298.15 K.

Fig. 2. Calculated refractive index (◊ A-B, ◊ D-G, Δ Nw, • L-L) versus experimental refractive index (continuous line) at 298.15 K.

Table 9
VALUES OF STANDARD DEVIATION OF MIXING RULES

| Temperature / K | α 10^4 |
|-----------------|--------|
|                 | A-B    | D-G    | Nw     | L-L    |
| 293.15          | 9.23   | 9.25   | 9.44   | 9.12   |
| 298.15          | 8.72   | 8.72   | 8.80   | 8.72   |
| 303.15          | 7.74   | 7.74   | 7.87   | 7.70   |

Table 8
VALUES OF STANDARD DEVIATION OF MIXING RULES

| A-B | D-G | Nw | L-L |
|-----|-----|----|-----|
| 293.15 | 9.23 | 9.25 | 9.44 | 9.12 |
| 298.15 | 8.72 | 8.72 | 8.80 | 8.72 |
| 303.15 | 7.74 | 7.74 | 7.87 | 7.70 |

Modeling refractive index data

The refractive indices were compared with the predicted results from the mixing rules proposed by Arago-Biot, Dale-Glastone, Newton and Lorentz-Lorenz [26-30]:

Arago - Biot (A-B):

\[ n_D = n_{D1}\phi_1 + n_{D2}\phi_2 + n_{D3}\phi_3 \]  \hspace{1cm} (9)

Dale - Glastone (D-G):

\[ n_D - 1 = (n_{D1} - 1)\phi_1 + (n_{D2} - 1)\phi_2 + (n_{D3} - 1)\phi_3 \]  \hspace{1cm} (10)

Newton (Nw):

\[ n_D - 1 = (n_{D1} - 1)\phi_1 + (n_{D2} - 1)\phi_2 + (n_{D3} - 1)\phi_3 \]  \hspace{1cm} (11)

Lorentz - Lorenz (L-L):

\[ \frac{n_D - 1}{n_D + 2} = \left(\frac{n_{D1} - 1}{n_{D1} + 2}\right)\phi_1 + \left(\frac{n_{D2} - 1}{n_{D2} + 2}\right)\phi_2 + \left(\frac{n_{D3} - 1}{n_{D3} + 2}\right)\phi_3 \]  \hspace{1cm} (12)

where \( n_{D1}, n_{D2}, n_{D3} \) are the refractive indices of the solution, of component 1, 2 and 3 respectively, and \( \phi_1, \phi_2 \), and \( \phi_3 \) are the volume fractions for component 1, 2 and 3 respectively.

Table 5 shows the standard deviation values calculated with the equation 5, where \( X_{exp} \) is the experimental refractive index and \( X_{calc} \) is the calculated refractive index. Figure 2 shows experimental and calculated values (equations 9-12) of refractive indices at 298.15 K.

From the data presented in table 8, it can be noticed that the Lorentz-Lorenz equation shows the lowest values of the standard deviation for 293.15 and 303.15 K. For 298.15 K the Arago-Biot, Dale-Glastone and Lorentz-Lorenz equations have the same standard deviation value. These results show the Lorentz-Lorenz is the best equation to estimate the refractive index of this ternary system.
Thermodynamic functions of activation

The energies of activation of viscous flow were calculated with equation:

$$ \eta = \frac{h}{V} e^{\frac{\Delta G^*}{RT}} $$

(13)

$$ \Delta G^* = \Delta H^* - T \Delta S^* $$

(14)

where: $\eta$ is viscosity of a liquid mixtures, $h$ is Planck’s constant, $V$ is Avogadro’s number, $R$ is the molar volume of the solution, $R$ is general gas constant, $T$ is temperature, $\Delta G^*$, $\Delta H^*$ and $\Delta S^*$ are the molar Gibbs energy, enthalpy and entropy of activation of viscous flow.

The plots of $ln(\eta V/hN)$ vs $1/T$ are linear in the temperature range 293.15 to 303.15 K and the values of $\Delta H^*$ and $\Delta S^*$ were obtained by the corresponding slopes and the intercepts. The values of $\Delta G^*$ were calculated with equation 14. The values of thermodynamic functions of activation of viscous flow as a function of composition are presented in table 9.

The values of $\Delta G^*$ and $\Delta H^*$ are positive for the ternary system of cyclohexane + cyclohexanol + cyclohexanone suggesting specific interactions, like H-bonding, between solution components. These values increase with the concentration range. The values of $\Delta S^*$ for cyclohexanol and for the solutions concentrated in alcohol show a less overall molecular order due to activated complex formation for viscous flow.

Conclusions

The densities, viscosities and refractive indices of ternary mixtures of cyclohexane + cyclohexanol + cyclohexanone were measured experimentally at three temperatures (293.15, 298.15 and 303.15 K) over the entire composition range. The density and viscosity of the solutions studied in this paper can be correctly estimated at different temperatures using a linear equations and Guzman equation respectively.

Grunberg-Nissan with three parameters and four parameters and Herc-Brewer models have been used to calculate viscosity coefficients and these were compared with experimental data for the ternary mixtures. The results of these correlations indicate that Herc-Brewer model is the best to describe viscosities of the ternary mixtures. Four mixing rules were tested to estimate the refractive index and these results were compared with the experimental values. The best results were obtained using the Lorentz-Lorenz equation. The energies of activation of viscous flow were calculated. The values of $\Delta H^*$ and $\Delta G^*$ are positive at all the temperatures and in the whole concentration range. The values of $\Delta S^*$ are positive for cyclohexanol and solutions concentrated in cyclohexanol and negative for cyclohexane, cyclohexanone and solutions diluted in alcohol.

References

1. SHARMA, V.K., DUA, R., SHARMA, D., J. Chem. Thermodynamics, 78, no. 11, 2014, p. 241
2. CRISCIU, A., SECUJANU, C., FEROIU, V., Rev. Chim. (Bucharest), 65, no. 1, 2014, p. 76
3. BUDANU, M.M., RADU, S., DUMITRESCU, V., Rev. Chim. (Bucharest), 61, no. 3, 2010, p. 322
4. ZHANG, Z., JIA, P., HUANG, D., DU, M., Lv.Y., LI, W., J. Chem. Eng. Data, 58, no. 11, 2013, p. 3054
5. PATNAIK, P., A Comprehensive Guide to the Hazardous Properties of Chemical Substances, third ed., John Wiley & Sons, New Jersey, USA, 2007
6. ALI, A., ABIDA, HYDER, S., Phys. Chem. Liq., 42, no. 4, 2004, p. 411
7. CIOCIRLAN, O., TEOODORESCU, M., DRAGOESCU, D., IULIAN, O., BARHALA, A., J. Chem. Eng. Data, 55, no. 9, 2010, p. 3891
8. RAFIEE, H.R., RANJ BAR, S., POURSALMAN, F., J. Chem. Thermodyn., 54, no. 11, 2012, p. 266
9. KUMARI, P.G., VENKATESU, P., HOFMAN, T., RAO, M.V.P., J. Chem. Eng. Data, 55, no. 1, 2010, p. 69
10. LI, G., LI, N., WANG, X., SHENG, X., LI, S., WANG, A., CONG, Y., WANG, X., ZHANG, T., Energy Fuel, 28, no. 8, 2014, p. 5112
11. LI, J., XU, Z., ZHANG, J., ZHANG, Y., XU, H., Journal of Chemical Thermodynamics, 39, no. 1, 2007, p. 28
12. ZHANG, N., ZHANG, J., ZHANG, Y., BAI, J., HUO, T. and WEI, X., Fluid Phase Equilibria, 311, 2012, p. 7
13. WEISSBERGER, A., Physical methods of Organic Chemistry, Interscience Publishers Inc, (New York), 1959
14. NAIN, A.K., ANSARI, S., and ALI, A., J. Solution Chem., 43, no. 4, 2014, p. 1032
15. YANG, C., LIU, Z., LAI, H., MA, P., J. Chem. Thermodynamics, 39, no. 1, 2007, p. 28
16. RIDDIICH, J.A., BUNGER, W.B., SAKANO, T.K., Organic Solvent, Wiley-Interscience, New York, 1986
17. BENSON, G.C., MURAKAMI, S., JONES, D.E.G., J. Chem. Thermodynamics, 5, no. 5, 1971, p. 719
18. ALI, A., NAIN, A.K., CHAND, D., LAL, B., Phys. Chem. Liq., 45, no. 1, 2007, p. 79
19. REDDY RAYAPA, K., KUMAR KARUNA BALA, D., RAO SRINIVASA, G., ANILA, P., RAMBABU, C., Thermochimica Acta, 590, 2014, p. 116
20. PALAIOLIOGOU, M.M., ARIANAS, G.K., TSIERKEYOS, N.G., J. Solution Chem., 35, no. 11, 2006, p. 1551
21. LANGE, N.A., Handbook of Chemistry, McGraw Hill, New York, 1973
22. MACQUEILIN, J., HUSSON, P., PADUA, A.A.H & MAJER, V., Green Chem., 8, no. 2, 2006, p. 162
23. MARQUARDT, D.W., J. Soc. Indust. Appl. Math., 11, no. 2, 1963, p. 431
24. GRUNBERG, L., NISSAN, A.H., Nature, 164, no. 41751949, p. 799
25. HERIC, E. L., BREWER, J. G., J. Chem. Eng. Data, 12, 1967, p. 574
26. ARAGO, D.J., BIOT, J.B., Mem. Acad. Fr., 15, 1806, p. 7
27. DALE, D. and GLADSTONE, F., Philos. Trans. R. Soc., 148, 1858, p. 887
28. KURZ, S., and WARD, A.L.J., Franklin Inst., 222, 1936, p. 563
29. LORENZ, H.A., Weid. Ann., 9, 1880, p. 641
30. LORENZ, L., Weid. Ann., 11, 1880, p. 70.

Manuscript received: 24.05.2018