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Cezary M. Kinart^a; Magdalena Klimczak^a; Marta Maj^a

^a Department of Physical Chemistry of Liquids, University of Łódź, Pomorska, Poland

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Viscosity of binary mixtures of 2-ethoxyethanol with ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol systems at $T = (293.15, 298.15 \text{ and } 303.15) \text{ K}$

Cezary M. Kinart*, Magdalena Klimczak and Marta Maj

Department of Physical Chemistry of Liquids, University of Łódź, Pomorska, Poland

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Viscosities, at $T=293.15, 298.15$ and 303.15 K , in the binary mixtures of 2-ethoxyethanol with ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol have been measured as a function of composition. From the experimental data the deviations in the viscosity have been calculated. The viscosity data, at $T=298.15 \text{ K}$, were correlated with equations of Hind *et al.*, Grunberg and Nissan, and Frenkel. The results are discussed in terms of intermolecular interactions and structural properties of studied binary mixtures.

Keywords: 2-ethoxyethanol; ethylene glycol; diethylene glycol; triethylene glycol; tetraethylene glycol; viscosity

1. Introduction

This article is a continuation of our studies on the thermodynamic and structural properties of some mixtures of glycols with alkoxyethanols [1–4]. In the present work, we have measured the viscosity (η) over the entire composition range, at $T=293.15, 298.15$ and 303.15 K , for binary mixtures of 2-ethoxyethanol (EE) with ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG) and tetraethylene glycol (TETRAEG).

These solvents have found a wide variety of applications in the petroleum, cosmetic, textile, pharmaceutical and other industries [5–10]. The study of the thermodynamic and transport properties of binary mixtures is significant for many purposes, one of which is to obtain information on molecular features of the studied mixtures [1–4]. The characterisation of the mixtures through their thermodynamic and transport properties is fundamentally important to understand their intermolecular interactions and internal structures, as well as in practical applications.

Therefore, we have decided to carry out the measurements of viscosity in these mixtures. From these results, the deviation of viscosity ($\Delta\eta$), at $T=293.15, 298.15$ and 303.15 K , from a mole fraction average have been calculated. These quantities have been fitted to the Redlich–Kister equation [11] to obtain the binary coefficients and standard deviations. Furthermore, the experimental results have been used to describe the nature of intermolecular interactions.

*Corresponding author. Email: ckinart@uni.lodz.pl

Table 1. Densities and relative permittivities of pure components, at $T=298.15$ K.

| Solvent | η (mPa s) | |
|---------|----------------|------------------------------------------------------|
| | This work | Literature |
| EE | 1.848 | 2.054 [24] 1.784 [25] 1.850 [26] 2.077 [27] |
| EG | 17.131 | 14.820 [28] |
| DEG | 29.978 | 30.012 [28] 30.000 [26] |
| TEG | 34.392 | 34.398 [28] |
| TETRAEG | 44.451 | 44.032 [29] |

2. Experimental

2.1. Materials

The following materials with mole fraction purity as stated were used: EE (Aldrich, purum, $GC \geq 0.995$ mole fraction), EG (Fluka, Switzerland, puriss. anhydrous, $GC > 0.99$ mole fraction), DEG (Fluka, Switzerland, puriss. p.a., $GC \geq 0.995$ mole fraction), TEG (Fluka, Switzerland, puriss. anhydrous, $GC > 0.99$ mole fraction) and TETRAEG (Fluka, Switzerland, purum, $GC \geq 0.99$ mole fraction). All glycols and EE were further purified by the methods described by us previously [1–4]. The mixtures were prepared using a Sartorius balance. Conversion to molar quantities was based on the relative atomic mass table of 1985, issued by IUPAC in 1986. The maximum estimated error in the mole fractions is $\pm 1 \times 10^{-4}$. Liquids were stored in a dry box over phosphorus pentoxide and degassed by ultrasound just before the experiment. Experimental viscosities for the pure solvents, at $T = 298.15$ K, are compared with values available in the literature and listed in Table 1. The differences between the measured and literature values can be ascribed to different measurement methods used, and to the different purification procedures employed by other authors [12].

2.2. Measurements

The flow times of the mixtures and the pure liquids were measured in a ViscoClock (made by Schott), equipped with an Ubbelohde capillary viscometer. Double distilled, deionised and degassed water with a specific conductance of $1 \times 10^{-9} \text{ s m}^{-1}$ was used for the calibration. The time measurement tolerance was $\pm 0.005\%$, and the display accuracy was ± 0.01 s. The uncertainty in the viscosity measurements was ± 0.001 mPa s. In all the viscosimetric property measurements, a Haake model DC-30 thermostat was used at a constant digital temperature control of ± 0.01 K.

3. Results and discussion

The experimental viscosities (η) obtained from the measurements of the pure solvents and for the binary mixtures, at $T = 293.15$, 298.15 and 303.15 K, are summarised in Table 2.

Table 2. Viscosities (η) and deviations in the viscosity ($\Delta\eta$) for {EE (1) + EG (2), EE (1) + DEG (2), EE (1) + TEG (2), and EE (1) + TETRAEG (2)} binary mixtures as a function of the mole fraction of EE (x_1), at $T=293.15, 298.15$ and 303.15 K.

| $T=293.15$ K | | $T=298.15$ K | | $T=303.15$ K | |
|-------------------|----------------------------|--------------|----------------------------|--------------|----------------------------|
| x_1 | $\eta(\text{mPa s})$ | x_1 | $\eta(\text{mPa s})$ | x_1 | $\eta(\text{mPa s})$ |
| Panel A: EE + EG | | | | | |
| 0.0000 | 21.179 | 0.0000 | 17.131 | 0.0000 | 13.533 |
| 0.0582 | 18.482 | 0.0423 | 15.822 | 0.0596 | 12.402 |
| 0.0952 | 16.678 | 0.1127 | 13.262 | 0.1011 | 11.292 |
| 0.2037 | 11.814 | 0.1983 | 10.122 | 0.1976 | 8.571 |
| 0.3098 | 7.965 | 0.2953 | 7.192 | 0.3002 | 5.937 |
| 0.4062 | 5.445 | 0.3988 | 4.883 | 0.3989 | 4.122 |
| 0.4503 | 4.568 | 0.4532 | 4.022 | 0.4504 | 3.447 |
| 0.5003 | 3.813 | 0.5005 | 3.474 | 0.4926 | 2.988 |
| 0.5413 | 3.301 | 0.5429 | 3.085 | 0.5502 | 2.554 |
| 0.5988 | 2.777 | 0.5930 | 2.739 | 0.6034 | 2.237 |
| 0.6952 | 2.401 | 0.6905 | 2.349 | 0.7013 | 1.974 |
| 0.8031 | 2.264 | 0.8044 | 2.188 | 0.8026 | 1.954 |
| 0.9002 | 2.143 | 0.8963 | 2.021 | 0.8923 | 1.933 |
| 0.9508 | 2.121 | 0.9496 | 1.940 | 0.9401 | 1.883 |
| 1.0000 | 2.142 | 1.0000 | 1.848 | 1.0000 | 1.646 |
| Panel B: EE + EG | | | | | |
| x_1 | $\Delta\eta(\text{mPa s})$ | x_1 | $\Delta\eta(\text{mPa s})$ | x_1 | $\Delta\eta(\text{mPa s})$ |
| 0.0000 | 0.000 | 0.0000 | 0.000 | 0.0000 | 0.000 |
| 0.0582 | -1.589 | 0.0423 | -0.663 | 0.0596 | -0.423 |
| 0.0952 | -2.689 | 0.1127 | -2.147 | 0.1011 | -1.039 |
| 0.2037 | -5.487 | 0.1983 | -3.978 | 0.1976 | -2.613 |
| 0.3098 | -7.316 | 0.2953 | -5.426 | 0.3002 | -4.028 |
| 0.4062 | -8.001 | 0.3988 | -6.153 | 0.3989 | -4.669 |
| 0.4503 | -8.039 | 0.4532 | -6.183 | 0.4504 | -4.732 |
| 0.5003 | -7.842 | 0.5005 | -6.008 | 0.4926 | -4.689 |
| 0.5413 | -7.573 | 0.5429 | -5.749 | 0.5502 | -4.439 |
| 0.5988 | -7.003 | 0.5930 | -5.329 | 0.6034 | -4.123 |
| 0.6952 | -5.543 | 0.6905 | -4.229 | 0.7013 | -3.223 |
| 0.8031 | -3.626 | 0.8044 | -2.649 | 0.8026 | -2.038 |
| 0.9002 | -1.899 | 0.8963 | -1.412 | 0.8923 | -0.993 |
| 0.9508 | -0.958 | 0.9496 | -0.678 | 0.9401 | -0.475 |
| 1.0000 | 0.000 | 1.0000 | 0.000 | 1.0000 | 0.000 |
| Panel C: EE + DEG | | | | | |
| x_1 | $\eta(\text{mPa s})$ | x_1 | $\eta(\text{mPa s})$ | x_1 | $\eta(\text{mPa s})$ |
| 0.0000 | 38.816 | 0.0000 | 29.978 | 0.0000 | 21.875 |
| 0.0582 | 33.167 | 0.0511 | 26.447 | 0.0643 | 18.694 |
| 0.0952 | 30.246 | 0.1023 | 23.406 | 0.0932 | 17.445 |
| 0.2037 | 23.278 | 0.2003 | 18.573 | 0.2072 | 13.228 |
| 0.3098 | 18.212 | 0.2998 | 14.699 | 0.3008 | 10.558 |
| 0.4062 | 14.482 | 0.3988 | 11.606 | 0.4001 | 8.317 |
| 0.4503 | 13.026 | 0.4514 | 10.245 | 0.4496 | 7.372 |
| 0.5003 | 11.500 | 0.4998 | 9.068 | 0.4939 | 6.612 |
| 0.5413 | 10.372 | 0.5476 | 8.079 | 0.5508 | 5.751 |

(continued)

Table 2. Continued.

| $T = 293.15 \text{ K}$ | | $T = 298.15 \text{ K}$ | | $T = 303.15 \text{ K}$ | |
|------------------------|----------------------------|------------------------|----------------------------|------------------------|----------------------------|
| x_1 | $\eta(\text{mPa s})$ | x_1 | $\eta(\text{mPa s})$ | x_1 | $\eta(\text{mPa s})$ |
| 0.5988 | 8.935 | 0.5996 | 7.096 | 0.5913 | 5.201 |
| 0.6952 | 6.844 | 0.6983 | 5.447 | 0.7010 | 3.930 |
| 0.8031 | 4.921 | 0.7991 | 4.050 | 0.7959 | 3.051 |
| 0.9002 | 3.465 | 0.8820 | 3.061 | 0.8990 | 2.267 |
| 0.9508 | 2.759 | 0.9500 | 2.337 | 0.9218 | 2.117 |
| 1.0000 | 2.142 | 1.0000 | 1.848 | 1.0000 | 1.646 |
| Panel D: EE + DEG | | | | | |
| x_1 | $\Delta\eta(\text{mPa s})$ | x_1 | $\Delta\eta(\text{mPa s})$ | x_1 | $\Delta\eta(\text{mPa s})$ |
| 0.0000 | 0.000 | 0.0000 | 0.000 | 0.0000 | 0.000 |
| 0.0582 | -3.515 | 0.0511 | -2.094 | 0.0643 | -1.880 |
| 0.0952 | -5.079 | 0.1023 | -3.694 | 0.0932 | -2.545 |
| 0.2037 | -8.068 | 0.2003 | -5.771 | 0.2072 | -4.456 |
| 0.3098 | -9.242 | 0.2998 | -6.846 | 0.3008 | -5.232 |
| 0.4062 | -9.437 | 0.3988 | -7.154 | 0.4001 | -5.464 |
| 0.4503 | -9.276 | 0.4514 | -7.035 | 0.4496 | -5.408 |
| 0.5003 | -8.968 | 0.4998 | -6.831 | 0.4939 | -5.272 |
| 0.5413 | -8.592 | 0.5476 | -6.495 | 0.5508 | -4.982 |
| 0.5988 | -7.921 | 0.5996 | -6.015 | 0.5913 | -4.713 |
| 0.6952 | -6.476 | 0.6983 | -4.888 | 0.7010 | -3.764 |
| 0.8031 | -4.442 | 0.7991 | -3.449 | 0.7959 | -2.724 |
| 0.9002 | -2.337 | 0.8820 | -2.106 | 0.8990 | -1.422 |
| 0.9508 | -1.187 | 0.9500 | -0.918 | 0.9218 | -1.111 |
| 1.0000 | 0.000 | 1.0000 | 0.000 | 1.0000 | 0.000 |
| Panel E: EE + TEG | | | | | |
| x_1 | $\eta(\text{mPa s})$ | x_1 | $\eta(\text{mPa s})$ | x_1 | $\eta(\text{mPa s})$ |
| 0.0000 | 41.010 | 0.0000 | 34.392 | 0.0000 | 29.244 |
| 0.0493 | 36.700 | 0.0425 | 31.400 | 0.0543 | 26.387 |
| 0.1039 | 32.108 | 0.1132 | 26.577 | 0.0954 | 24.223 |
| 0.1964 | 25.210 | 0.1980 | 21.561 | 0.2034 | 19.005 |
| 0.3004 | 18.992 | 0.2956 | 16.854 | 0.2991 | 15.107 |
| 0.3949 | 14.527 | 0.3992 | 12.840 | 0.4003 | 11.778 |
| 0.4468 | 12.490 | 0.4535 | 11.089 | 0.4492 | 10.391 |
| 0.5005 | 10.662 | 0.5008 | 9.696 | 0.5007 | 9.084 |
| 0.5512 | 9.194 | 0.5433 | 8.635 | 0.5429 | 8.086 |
| 0.6003 | 7.883 | 0.5935 | 7.463 | 0.5978 | 6.967 |
| 0.7017 | 5.752 | 0.6900 | 5.545 | 0.6987 | 5.187 |
| 0.7946 | 4.246 | 0.8038 | 3.871 | 0.8008 | 3.732 |
| 0.9032 | 2.957 | 0.8966 | 2.774 | 0.9005 | 2.597 |
| 0.9410 | 2.603 | 0.9500 | 2.248 | 0.9500 | 2.081 |
| 1.0000 | 2.142 | 1.0000 | 1.848 | 1.0000 | 1.646 |
| Panel F: EE + TEG | | | | | |
| x_1 | $\Delta\eta(\text{mPa s})$ | x_1 | $\Delta\eta(\text{mPa s})$ | x_1 | $\Delta\eta(\text{mPa s})$ |
| 0.0000 | 0.000 | 0.0000 | 0.000 | 0.0000 | 0.000 |
| 0.0493 | -2.394 | 0.0425 | -1.615 | 0.0543 | -1.358 |

(continued)

Table 2. Continued.

| $T = 293.15 \text{ K}$ | | $T = 298.15 \text{ K}$ | | $T = 303.15 \text{ K}$ | |
|------------------------|----------------------------|------------------------|----------------------------|------------------------|----------------------------|
| x_1 | $\eta(\text{mPa s})$ | x_1 | $\eta(\text{mPa s})$ | x_1 | $\eta(\text{mPa s})$ |
| 0.1039 | -4.864 | 0.1132 | -4.147 | 0.0954 | -2.388 |
| 0.1964 | -8.166 | 0.1980 | -6.378 | 0.2034 | -4.626 |
| 0.3004 | -10.342 | 0.2956 | -7.926 | 0.2991 | -5.882 |
| 0.3949 | -11.134 | 0.3992 | -8.573 | 0.4003 | -6.419 |
| 0.4468 | -11.154 | 0.4535 | -8.554 | 0.4492 | -6.456 |
| 0.5005 | -10.895 | 0.5008 | -8.408 | 0.5007 | -6.342 |
| 0.5512 | -10.392 | 0.5433 | -8.089 | 0.5429 | -6.175 |
| 0.6003 | -9.794 | 0.5935 | -7.630 | 0.5978 | -5.779 |
| 0.7017 | -7.984 | 0.6900 | -6.375 | 0.6987 | -4.774 |
| 0.7946 | -5.879 | 0.8038 | -4.343 | 0.8008 | -3.412 |
| 0.9032 | -2.947 | 0.8966 | -2.449 | 0.9005 | -1.795 |
| 0.9410 | -1.832 | 0.9500 | -1.240 | 0.9500 | -0.945 |
| 1.0000 | 0.000 | 1.0000 | 0.000 | 1.0000 | 0.000 |
| Panel G: EE + TETRAEG | | | | | |
| x_1 | $\eta(\text{mPa s})$ | x_1 | $\eta(\text{mPa s})$ | x_1 | $\eta(\text{mPa s})$ |
| 0.0000 | 53.236 | 0.0000 | 44.451 | 0.0000 | 35.686 |
| 0.0502 | 47.889 | 0.0686 | 38.727 | 0.0528 | 32.257 |
| 0.0969 | 43.092 | 0.1055 | 35.935 | 0.1002 | 29.431 |
| 0.2063 | 33.375 | 0.1983 | 29.367 | 0.1959 | 24.271 |
| 0.2971 | 26.658 | 0.2962 | 23.471 | 0.3050 | 19.161 |
| 0.4006 | 20.217 | 0.3972 | 18.272 | 0.4084 | 14.963 |
| 0.4466 | 17.747 | 0.4507 | 15.905 | 0.4513 | 13.359 |
| 0.5031 | 15.004 | 0.5008 | 13.909 | 0.4997 | 11.720 |
| 0.5526 | 12.919 | 0.5475 | 12.210 | 0.5489 | 10.244 |
| 0.5998 | 11.107 | 0.5997 | 10.475 | 0.5937 | 9.006 |
| 0.7001 | 7.904 | 0.7000 | 7.546 | 0.6994 | 6.489 |
| 0.7995 | 5.434 | 0.7998 | 5.214 | 0.8006 | 4.511 |
| 0.9000 | 3.553 | 0.8932 | 3.431 | 0.9014 | 2.903 |
| 0.9500 | 2.792 | 0.9502 | 2.517 | 0.9481 | 2.266 |
| 1.0000 | 2.142 | 1.0000 | 1.848 | 1.0000 | 1.646 |
| Panel H: EE + TETRAEG | | | | | |
| x_1 | $\Delta\eta(\text{mPa s})$ | x_1 | $\Delta\eta(\text{mPa s})$ | x_1 | $\Delta\eta(\text{mPa s})$ |
| 0.0000 | 0.000 | 0.0000 | 0.000 | 0.0000 | 0.000 |
| 0.0502 | -2.782 | 0.0686 | -2.801 | 0.0528 | -1.632 |
| 0.0969 | -5.193 | 0.1055 | -4.021 | 0.1002 | -2.844 |
| 0.2063 | -9.320 | 0.1983 | -6.636 | 0.1959 | -4.747 |
| 0.2971 | -11.398 | 0.2962 | -8.361 | 0.3050 | -6.143 |
| 0.4006 | -12.551 | 0.3972 | -9.257 | 0.4084 | -6.821 |
| 0.4466 | -12.670 | 0.4507 | -9.345 | 0.4513 | -6.965 |
| 0.5031 | -12.527 | 0.5008 | -9.206 | 0.4997 | -6.956 |
| 0.5526 | -12.082 | 0.5475 | -8.916 | 0.5489 | -6.757 |
| 0.5998 | -11.483 | 0.5997 | -8.427 | 0.5937 | -6.470 |
| 0.7001 | -9.561 | 0.7000 | -7.083 | 0.6994 | -5.389 |
| 0.7995 | -6.952 | 0.7998 | -5.163 | 0.8006 | -3.923 |
| 0.9000 | -3.698 | 0.8932 | -2.967 | 0.9014 | -2.099 |
| 0.9500 | -1.905 | 0.9502 | -1.453 | 0.9481 | -1.147 |
| 1.0000 | 0.000 | 1.0000 | 0.000 | 1.0000 | 0.000 |

Table 3. Coefficients β_j and standard deviations $\sigma(\ln \eta)$ of Equation (1) for {EE (1)+EG (2), EE (1)+DEG (2), EE (1)+TEG (2) and EE (1)+TETRAEG (2)} binary mixtures, at $T=293.15, 298.15, \text{ and } 303.15 \text{ K}$.

| $T(\text{K})$ | β_0 | β_1 | β_2 | β_3 | β_4 | $\sigma(\ln \eta) \times 10^3$ |
|-----------------------|-----------|-----------|-----------|-----------|-----------|--------------------------------|
| Panel A: EE + EG | | | | | | |
| 293.15 | 3.0280 | -1.0127 | -11.5296 | 16.9080 | -6.6267 | 10.6 |
| 298.15 | 2.8266 | -0.8683 | -11.9085 | 18.7781 | -8.2112 | 8.5 |
| 303.15 | 2.5788 | 0.1173 | -15.8746 | 24.7238 | -11.0205 | 9.1 |
| Panel B: EE + DEG | | | | | | |
| 293.15 | 3.6511 | -2.4633 | -0.1914 | 1.3615 | -1.5867 | 8.7 |
| 298.15 | 3.3962 | -2.2739 | -0.7863 | 2.0200 | -1.7365 | 4.2 |
| 303.15 | 3.0847 | -2.4145 | -0.1056 | 0.4401 | -0.5055 | 8.1 |
| Panel C: EE + TEG | | | | | | |
| 293.15 | 3.7173 | -2.2351 | -0.8738 | 0.3578 | -0.1079 | 3.1 |
| 298.15 | 3.5395 | -2.2013 | -0.9561 | 0.9877 | -0.7580 | 3.0 |
| 303.15 | 3.3752 | -1.7863 | -2.1169 | 3.0252 | -1.9969 | 3.4 |
| Panel D: EE + TETRAEG | | | | | | |
| 293.15 | 3.9728 | -2.0065 | -1.3681 | 1.2864 | -1.1187 | 3.2 |
| 298.15 | 3.7904 | -1.7752 | -1.9472 | 2.9383 | -2.3873 | 2.9 |
| 303.15 | 3.5671 | -1.5623 | -2.3639 | 3.4142 | -2.5480 | 5.7 |

The variations of the viscosity with binary composition were studied by using the following equation [13,14]:

$$\ln \eta(x_1) = \sum_{j=0}^4 \beta_j \cdot x_1^j, \tag{1}$$

which could be fitted to the experimental data, at $T=293.15, 298.15 \text{ and } 303.15 \text{ K}$, using a least-squares method. The β_j coefficients of this fitting procedure are listed in Table 3, along with the standard deviations $\sigma(\ln \eta)$ for each binary mixture.

The goodness-of-fit of this procedure is ascertained by a mean deviation $\overline{\Delta\eta} = \pm 9.6 \times 10^{-3} \text{ mPa s}$ for (EE + EG), $\overline{\Delta\eta} = \pm 4.9 \times 10^{-3} \text{ mPa s}$ for (EE + DEG), $\overline{\Delta\eta} = \pm 2.1 \times 10^{-3} \text{ mPa s}$ for (EE + TEG), and $\overline{\Delta\eta} = \pm 3.7 \times 10^{-3} \text{ mPa s}$ for (EE + TETRAEG) binary liquid mixtures.

From the measured viscosities the deviations of viscosity ($\Delta\eta$) of the studied mixtures, at $T=293.15, 298.15 \text{ and } 303.15 \text{ K}$, were fitted to the equation:

$$\Delta\eta = \eta - (x_1 \times \eta_1 + x_2 \times \eta_2), \tag{2}$$

where η_1, η_2 and η are the viscosities of the EE, EGs and the mixtures, respectively.

The deviations of viscosity were fitted by a Redlich–Kister-type equation [11]:

$$\Delta\eta(\text{mPa s}) = x_1 \cdot (1 - x_1) \sum_{j=0}^4 a_j \cdot (2x_1 - 1)^j. \tag{3}$$

The parameters a_j of Equation (3) were evaluated by the least-squares method. The values of these parameters with standard deviation $\sigma(\Delta\eta)$ are summarised in Table 4.

Table 4. Coefficients a_j and standard deviations $\sigma(\Delta\eta)$ of Equation (3) for {EE (1)+EG (2), EE (1)+DEG (2), EE (1)+TEG (2) and EE (1)+TETRAEG (2)} binary mixtures, at $T=293.15$, 298.15, and 303.15 K.

| $T(K)$ | k_0 | k_1 | k_2 | k_3 | k_4 | $\sigma(\Delta\eta)$ (mPa s) |
|-----------------------|----------|---------|---------|-----------|---------|------------------------------|
| Panel A: EE + EG | | | | | | |
| 293.15 K | -31.4648 | 11.482 | 8.3603 | -7.8919 | 0.0158 | 0.037 |
| 298.15 K | -24.0675 | 9.9524 | 7.0596 | -9.8331 | 4.0326 | 0.026 |
| 303.15 K | -18.6646 | 5.9517 | 7.8151 | -8.1324 | 7.5545 | 0.020 |
| Panel B: EE + DEG | | | | | | |
| 293.15 K | -35.8627 | 15.4377 | -6.8623 | 7.7905 | -5.3864 | 0.022 |
| 298.15 K | -27.2878 | 11.5257 | -3.4304 | 1.8947 | -1.7654 | 0.012 |
| 303.15 K | -2.9691 | 8.5252 | -2.8528 | 0.7422 | -0.0987 | 0.007 |
| Panel C: EE + TEG | | | | | | |
| 293.15 K | -43.5341 | 14.6791 | -2.3042 | -4.4.9474 | 4.9580 | 0.027 |
| 298.15 K | -33.5377 | 10.9918 | -2.1962 | -2.5530 | 2.9517 | 0.039 |
| 303.15 K | -25.4012 | 7.3055 | -0.2272 | -4.0357 | 3.9283 | 0.021 |
| Panel D: EE + TETRAEG | | | | | | |
| 293.15 K | -50.0596 | 11.3995 | -0.6102 | -0.4667 | -1.1719 | 0.039 |
| 298.15 K | -36.8491 | 8.4084 | -0.2028 | -1.5457 | -0.1764 | 0.027 |
| 303.15 K | -27.7067 | 3.9698 | 2.7317 | 1.5878 | -4.0148 | 0.022 |

Standard deviation values were obtained from:

$$\sigma = \left[\frac{\sum (V_{\text{exptl}} - V_{\text{calcd}})^2}{n - p} \right]^{1/2}, \quad (4)$$

where n is the number of experimental points, p is the number of parameters, V_{exptl} and V_{calcd} are the experimental and calculated properties.

As suggested by other authors [13–16], the study of this structural parameter ($\Delta\eta$ for binary liquid systems represents a unique tool for investigating the formation of intermolecular complexes, and provides a valuable aid for determining their stoichiometry. The position of the relative minima or maxima in the plots of $\Delta\eta$ versus x_1 , could be taken as the true composition of these intermolecular complexes.

For reasons of clarity, only the variations of $\Delta\eta$ values as a function of the mole fraction of EE (x_1) at one temperature ($T=298.15$ K) for all studied mixtures are presented in Figure 1. The results (presented in Table 2 and Figure 1) indicate that $\Delta\eta$ is negative over the entire composition range for all studied systems. The values of $\Delta\eta$ become increasingly negative as the chain length of the glycol molecules (the number of oxyethylene groups $-\text{O}-\text{CH}_2-\text{CH}_2-$ in the glycol) increases and temperature decreases (Table 2), and are in the following order:

$$\Delta\eta_{\text{min}}(\text{EE} + \text{TETRAEG}) > \Delta\eta_{\text{min}}(\text{EE} + \text{TEG}) > \Delta\eta_{\text{min}}(\text{EE} + \text{DEG}) > \Delta\eta_{\text{min}}(\text{EE} + \text{EG}).$$

As is suggested in the literature, negative viscosity deviations from rectilinear dependence on mole fraction may also occur where dispersion forces are dominant, particularly for the systems having different molecular size [17–20]. This reveals that the strength of specific interaction is not the only factor influencing the viscosity deviation of the studied binary liquid mixtures. In these mixtures, the molecular size and shape of the components and dispersion forces also play an equally important role.

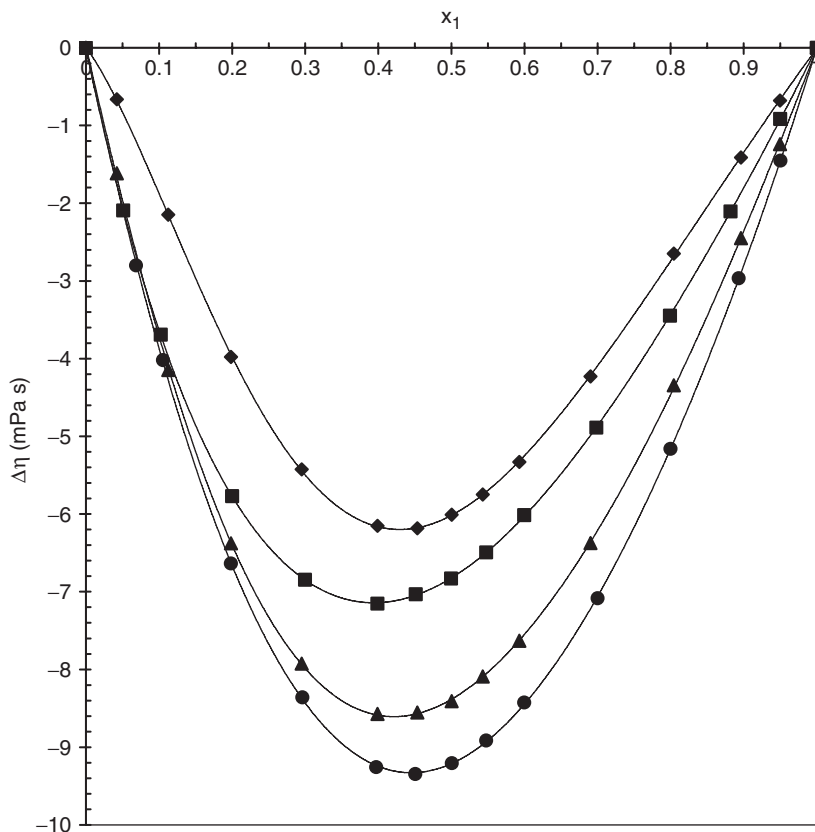


Figure 1. Plot of the deviation of the viscosity ($\Delta\eta$) against mole fraction EE (x_1) for {(◆) EE (1) + EG (2), (■) EE (1) + DEG (2), (▲) EE (1) + TEG (2) and (●) EE (1) + TETRAEG (2)} binary liquid mixtures, at $T = 298.15$ K.

Ethylene glycols and EE are a very interesting class of solvents, due to the presence of the oxy and hydroxyl groups in the same molecule, which allow self-association via intra- and intermolecular hydrogen bonds. The formation of intramolecular hydrogen bonds in EE and EGs is more favourable when the molecules of these solvents are in the *gauche* conformations. Probably, the addition of pure EE to EGs (or contrariwise) would disrupt the self-associated structure in EE and EGs causing the appearance in the solutions of free molecules. These free molecules may interact by dipole-dipole forces and/or intermolecular hydrogen bonds forming the mixed intermolecular complexes.

The same structural effects have been observed in binary mixtures of ME + polyEG [2]. Several semi-empirical equations have been used to estimate the viscosity of liquid mixtures in terms of pure component data.

The experimental viscosity data of analysed binary liquid mixtures, at $T = 298.15$ K, were further fitted to:

- the Hind *et al.* Equation [21]:

$$\eta = x_1^2 \cdot \eta_1 + x_2^2 + 2 \cdot x_1 \cdot x_2 \cdot H_{12}, \quad (5)$$

Table 5. Adjustable parameters and standard deviations of several semiempirical equations for {EE (1)+EG (2), EE (1)+DEG (2), EE (1)+TEG (2) and EE (1)+TETRAEG (2)} binary mixtures, at $T=298.15$ K.

| Equation | Values of the parameters | $\sigma \times 10^2$ |
|-----------------------|--------------------------|----------------------|
| Panel A: EE + EG | | |
| Grunberg–Nissan | $G_{12} = -1.1520$ | 0.56 |
| Hind <i>et al.</i> | $H_{12} = -2.0809$ | 0.76 |
| Frenkel | $F_{12} = 3.1630$ | 0.76 |
| Panel B: EE + DEG | | |
| Grunberg–Nissan | $G_{12} = 0.6555$ | 0.41 |
| Hind <i>et al.</i> | $H_{12} = 2.0449$ | 0.86 |
| Frenkel | $F_{12} = 10.3289$ | 0.42 |
| Panel C: EE + TEG | | |
| Grunberg–Nissan | $G_{12} = 0.7581$ | 0.13 |
| Hind <i>et al.</i> | $H_{12} = 1.2637$ | 0.69 |
| Frenkel | $F_{12} = 11.6465$ | 0.14 |
| Panel D: EE + TETRAEG | | |
| Grunberg–Nissan | $G_{12} = 1.5359$ | 0.55 |
| Hind <i>et al.</i> | $H_{12} = 4.6953$ | 0.72 |
| Frenkel | $F_{12} = 19.5351$ | 0.74 |

- the Grunberg and Nissan Equation [22]:

$$\eta = \exp(x_1 \cdot \ln \eta_1 + x_2 \cdot \ln \eta_2 + x_1 \cdot x_2 \cdot G_{12}), \quad (6)$$

where G_{12} is a parameter proportional to the interaction energy, and

- the Frenkel Equation [23]:

$$\ln \eta = \sum_{i=1}^n x_i^2 \cdot \eta_i + 2 \left[\sum_{i=1}^n \sum_{j>1}^n x_i \cdot x_j \cdot \ln F_{ij} \right], \quad (7)$$

where F_{ij} are the parameters representing binary 12 interactions.

To perform a numerical comparison of the correlating ability of Equations (5)–(7), we calculated the standard deviations (σ). The values of the parameters of Equations (5)–(7) were determined for the systems using a least-squares method, with equal weights assigned to each experimental datum. The correlation parameters and standard deviations (σ) for these equations are listed in Table 5. It is observed that the relation fit the Grunberg–Nissan experimental results better compared to the Hind and Frenkel equations, as the σ values for the Grunberg–Nissan latter equations are larger than the values for the equation in the studied binary mixtures.

In the studied mixtures, at all applied temperatures, an interesting relationship was observed between the values of the minimum of $\Delta\eta_{\min}$ plotted as a function of the number carbon atoms present in the studied EGs molecules (Figure 2). It was found that they lie along a straight line with an increasing slope with decreasing temperature.

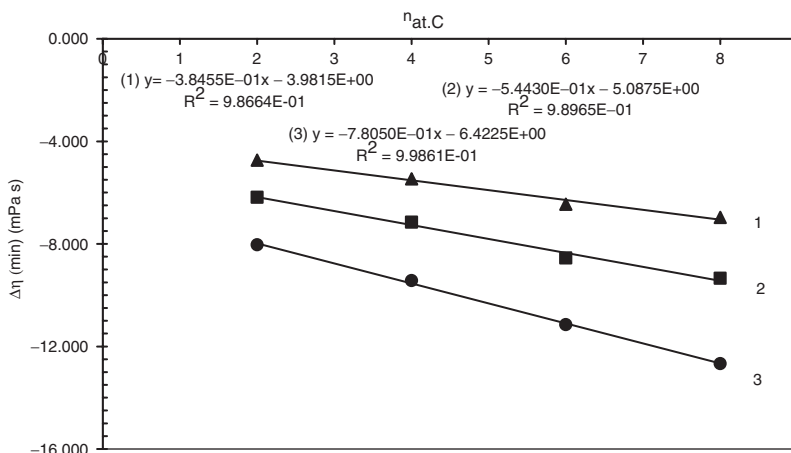


Figure 2. The $\Delta\eta_{\min}$ values plotted against the number of carbon atoms in the studied ethylene glycols for EE+EG, EE+DEG, EE+TEG and EE+TETRAEG binary mixtures, at (3) $T=293.15$ K, (2) $T=298.15$ K and (1) $T=303.15$ K.

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