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# Excess viscosities of binary mixtures of water with tetrahydrofuran & dioxane at 303.15 K

R Venkateswarlu, Pallagolla Rajasekhar & K S Reddy*

Department of Chemistry, Sri Venkateswara University, Tirupati 517 502

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Excess viscosities and partial molar excess viscosities of binary mixtures of water with tetrahydrofuran and dioxane have been computed from the viscosities and the densities of pure components and mixtures over the complete range of mol fraction. Excess properties are positive and their significance is discussed in terms of the molecular interactions in the mixtures.

Molecular interactions in the mixtures of tetrahydrofuran (THF) and dioxane with water have been thoroughly investigated in terms of excess thermodynamic properties[1-8], except in terms of excess viscosities. We report herein excess viscosities and partial molar excess viscosities for the title binary mixtures at 303.15 K.

Water, dioxane (E Merck) and THF (Reidel) were purified by literature methods. The purity of the samples was ascertained by comparing their densities and boiling points with the literature values[9]. Viscosities were measured with an Ostwald viscometer and the values were accurate to ± 0.5%, while densities were measured using a bicapillary pycnometer with an accuracy of $\pm 5 \times 10^{-5}$ g cm$^{-3}$. All the mixtures were prepared by weight.

Excess viscosities were calculated using Eq (1) and the values are given in Table 1.

$$\ln \eta^E = \ln \eta - [x_1 \ln \eta_1 + (1 - x_1) \ln \eta_2] \quad \ldots (1)$$

Excess viscosities are represented with a polynomial equation[10] of the form (2)

$$\ln \eta^E = \frac{x_1(1 - x_1)[a_1 + a_2(1 - 2x_1) + a_3(1 - 2x_1)^2]}{[1 + a_0(1 - 2x_1)]} \quad \ldots (2)$$

where $a_0$ is skewing constant and is calculated using Eq. (3)

$$a_0 = -2(1 - 2x_{1ext})/[1 + (1 - 2x_{1ext})^2] \quad \ldots (3)$$

In Eq. (3), $x_{1, ext}$ is the mol fraction corresponding to maximum $\ln \eta^E$. The parameters $a_1$, $a_2$ and $a_3$ are obtained by the method of least squares and are given in Table 2 along with standard deviation ($\sigma$). Partial molar excess viscosities for components 1 and 2 were calculated[11] and the results are included in Table 1.

The results presented in Table 1 reveal that the excess viscosities are positive over the whole range

Table 1—Mole fraction ($x_1$), density ($\rho$), viscosity ($\eta$), excess viscosity ($\ln \eta^E$) and partial molar excess viscosities of components 1 and 2 ($\ln \bar{\eta}_1^E$ & $\ln \bar{\eta}_2^E$) at 303.15 K

| $x_1$ | $\rho$ g·cm$^{-3}$ | $\eta$ cp | $\ln \eta^E$ | $\ln \bar{\eta}_1^E$ | $\ln \bar{\eta}_2^E$ |
|---|---|---|---|---|---|
| Tetrahydrofuran (1) + Water (2) | | | | | |
| 0.0000 | 0.99561 | 0.793 | — | — | — |
| 0.0485 | 0.98717 | 1.217 | 0.455 | 15.055 | −0.372 |
| 0.1010 | 0.97709 | 1.381 | 0.608 | 9.567 | −0.406 |
| 0.1479 | 0.96663 | 1.425 | 0.664 | 6.648 | −0.331 |
| 0.2006 | 0.95508 | 1.366 | 0.649 | 4.484 | −0.252 |
| 0.3276 | 0.93338 | 1.098 | 0.505 | 1.576 | −0.011 |
| 0.4903 | 0.91347 | 0.853 | 0.330 | 0.439 | 0.239 |
| 0.6398 | 0.89921 | 0.674 | 0.174 | 0.041 | 0.401 |
| 0.7728 | 0.88973 | 0.565 | 0.067 | −0.038 | 0.393 |
| 0.9015 | 0.88144 | 0.500 | 0.012 | −0.014 | 0.239 |
| 0.9491 | 0.87912 | 0.484 | 0.003 | −0.004 | 0.136 |
| 1.0000 | 0.87652 | 0.469 | — | — | — |
| Dioxane (1) + Water (2) | | | | | |
| 0.0000 | 0.99561 | 0.793 | — | — | — |
| 0.0495 | 1.01324 | 1.122 | 0.335 | 11.815 | −0.337 |
| 0.1010 | 1.02333 | 1.361 | 0.516 | 9.096 | −0.446 |
| 0.1464 | 1.02913 | 1.505 | 0.605 | 7.177 | −0.489 |
| 0.1964 | 1.03201 | 1.602 | 0.655 | 5.523 | −0.478 |
| 0.3401 | 1.03402 | 1.579 | 0.606 | 2.383 | −0.301 |
| 0.4812 | 1.03053 | 1.405 | 0.454 | 0.832 | 0.054 |
| 0.6535 | 1.02712 | 1.221 | 0.272 | 0.116 | 0.566 |
| 0.8065 | 1.02432 | 1.071 | 0.102 | −0.034 | 0.680 |
| 0.9033 | 1.02303 | 1.017 | 0.027 | −0.020 | 0.469 |
| 0.9495 | 1.02260 | 1.008 | 0.007 | −0.007 | 0.270 |
| 1.000 | 1.02190 | 1.014 | — | — | — |

Table 2—Skewing constant ($a_0$), least square parameters ($a_1$, $a_2$, $a_3$) and standard deviation ($\sigma \ln \eta^E$) at 303.15 K for the binary mixtures of water with THF and dioxane

| $a_0$ | $a_1$ | $a_2$ | $a_3$ | $\sigma(\ln \eta^E)$ |
|---|---|---|---|---|
| Tetrahydrofuran + Water | | | | |
| −0.9415 | 0.8922 | −0.4251 | 1.2517 | 0.037 |
| Dioxane + Water | | | | |
| −0.9396 | 0.5325 | −1.3441 | 1.8387 | 0.027 |

of mol fraction for the two systems. The plot of ln $\eta^E$ versus mol fraction is highly unsymmetrical and skewed towards water-rich region with maximum in ln $\eta^E$ at about $x_1 = 0.15$ and $x_1 = 0.2$ for the systems THF + water and dioxane + water respectively. This typical behaviour in water-rich region may be interpreted on the basis of enhancement of water-water interactions of hydrophobic nature and the presence of weak H-bonding between unlike molecules[12]. At higher values of $x_1$, the H-bonding in water may be broken and intercomponent H-bonding may become predominant. Further, the large values of ln $\tilde{\eta}_1^E$, in water-rich mixtures also support the above interpretation.

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