

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

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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<sup>1-8</sup>, 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<sup>9</sup>. Viscosities were measured with an Ostwald viscometer and the values were accurate to  $\pm 0.5\%$ , while densities were measured using a bicapillary pycnometer with an accuracy of  $\pm 5 \times 10^{-5} \text{ g cm}^{-3}$ . All the mixtures were prepared by weight.

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

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

Excess viscosities are represented with a polynomial equation<sup>10</sup> of the form (2)

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

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

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

In Eq. (3),  $x_{1, \text{ext}}$  is the mol fraction corresponding to maximum  $\ln \eta^E$ . The parameters  $a_1$ ,  $a_2$  and  $a_3$

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

| $x_1$                           | $\rho$<br>g·cm <sup>-3</sup> | $\eta$<br>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                |

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<sup>11</sup> 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

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<sup>12</sup>. 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  $\ln \eta^E$ , in water-rich mixtures also support the above interpretation.

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The inverse dependence of rate on periodate indicates the probable existence of a dissociated species in which the Ni(IV) moiety loses a periodate ligand forming monoperiodatnickelate(IV) (V).



This monoperiodatnickelate(IV), Ni(OH)<sub>2</sub>(L), is assumed to be the reactive species and its concentration is expected to be much less than that of diperiodatnickelate(IV).

As Ni(IV) has already been reported<sup>13</sup> to behave as a two electron oxidant, we assume here a two electron transfer from the alcoholic function to Ni(IV) species in the rate-determining step.

The possibility of involvement of alkoxide ion does not appear probable as effect of added salts on rate of reaction was negligible. The rates of reaction followed the order mandelic acid > glycollic acid > lactic acid indicating that electron withdrawing substituents at the  $\alpha$ -position increased the rate of oxidation. Hence the reaction is assumed to proceed through an adduct formation which decomposes in the slow step with the removal of a hydrogen probably as proton. This assumption re-

fractional rate of mandelic acid (pKa=3.4) and glycollic and lactic acids (pKa=3.8) were prepared and used as substrates. Other chemicals used were of A.R. B.D.H. grade. Diperiodatnickelate(IV) was prepared as reported by Ray<sup>14</sup> and standardized by method reported earlier. The progress of the reaction was followed by measuring the disappearance of Ni(IV) at 410 nm employing UV-visible beam spectrophotometer (Shimadzu 1601). Spectrophotometric studies showed that one mole of a substrate with one mole of substrate under kinetic conditions the oxidation products were identified as the corresponding keto acids by their characteristic spot tests.

Under the conditions [Ni(IV)] < [substrate] the plot of log absorbance versus time were linear ( $\lambda = 0.98$ ) indicating the order in [Ni(IV)] to be unity. From the slopes of such plots the pseudo-first order rate constants ( $k'$ ) were calculated. The plots of log  $k'$  versus log [substrate] were also linear ( $\lambda = 0.97$ ) with a unit slope in each case indicating order in [substrate] to be unity.

The rate of reaction was found to increase with increase in [OH<sup>-</sup>] and showed an inverse dependence on [periodate]. For instance, in the reaction with lactic acid at fixed [Ni(IV)], [lactic acid] and temperature (300 K) the rate constant ( $k'$ ) increased

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