

Measurement and Predict Thermo Physical Properties of Binary Liquid Mixtures at Various Temperatures Using Redlich-Kister Model

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Abstract Excess molar volume and viscosities are one of the important fundamental data for the design and optimization of chemical process. In this study, excess molar volume and viscosities of 1,4 Dioxane with two hydrocarbons Bromobenzene and Ethyl benzene have been measured over the entire range of composition at (303.15, 308.15, and 313.15) K. From experimentations excess volumes, V^E , and deviations in viscosities, $\Delta\eta$, are calculated. The calculated excess volumes, V^E and deviations in viscosities, $\Delta\eta$ exhibited positive and negative values respectively over the whole range of composition in both binary systems. The Redlich-Kister Model was used to correlate excess volumes, V^E , and deviations in viscosities, $\Delta\eta$, to derive the binary coefficients and standard deviations of these systems. The fitted outcomes and the calculated data clearly indicated that weak interactions present in two mixtures. It is mainly because of number and position of methyl groups exist in these aromatic hydrocarbons. It can conclude that the experimental values are predicted well by the Redlich-Kister Model with high degree of precision.

Keywords: Redlich-Kister Model, excess molar volume and viscosity measurement

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1. Introduction

The quantitative viscosity, excess molar volume and density data of liquid mixtures are required to solve many engineering problems, involve in chemical separations, heat transfer, mass transfer, and fluid flow are important from practical and theoretical points of view, for understanding liquid theory. The low polarity of 1, 4 Dioxane is interesting to study with hydrocarbon mixtures, for the type of interaction between the components of binary systems. 1,4 Dioxane commonly known as excellent aprotic solvent, it has a zero dipole moment and cyclic ether, that has an electron donor ability towards aromatic rings, it act like weak electron acceptors. 1, 4 Dioxane is used as a stabilizer in aluminium containers and solvent in inks and adhesives. There are few reports on density and viscosity data of 1, 4 Dioxane with hydrocarbon mixtures [1,2]. In our earlier paper, we had studied thermo physical properties of binary systems [2]. In the present paper, it has been reported density (ρ) and viscosity (η) of pure 1, 4 Dioxane, Bromo Benzene and Ethyl Benzene for the binary system constituted by these two chemicals at entire range of composition and temperature $T = (303.15 \text{ to } 313.15) \text{ K}$. With this data, the

excess molar volume and deviation in viscosity have been computed. These results have been fitted to the Redlich-Kister and polynomial equations. The Redlich-Kister was used to correlate the excess volumes, V^E , and deviations in viscosities, $\Delta\eta$, this analysis technique was used to derive the binary coefficients, estimated the standard deviation (σ) between the experimental and calculated data [4]. The variation of these parameters with the composition and temperature of the mixtures has been discussed in terms of the molecular interactions in these mixtures. The effect of the number and position of the methyl groups in these aromatic hydrocarbons on molecular interactions in these mixtures has also been discussed. A literature search showed that no measurements have been previously reported by using Redlich-Kister model for the mixtures studied in this paper.

2. Experimental Section

2.1. Materials

1, 4-Dioxane, Bromobenzene, Ethyl benzene, this were all supplied by M/s E.Merck Ltd. With the stated purities better than 99 %, were stored over molecular sieves (0.3 nm). 1, 4 Dioxane with purity of 99 % provided by Sigma-

Aldrich Chemicals and it was used without further purification. To minimize the contact of these reagents with moist air, the products were kept in sealed bottles in a desiccator. The purity of the substances were determined

by GLC. Densities and viscosities of pure substances and experimental values comparison with literature values are listed in Table 1 [1,2,3,4].

Table 1. Experimental Densities and viscosities of Pure Liquids with Literature Values at 303.15K

| Component | T(K) | $\rho/\text{g}\cdot\text{cm}^{-3}$ | | $\eta/(\text{m Pa s})$ | |
|---------------|--------|------------------------------------|--------|------------------------|--------|
| | | Lit | Exp | Lit | Exp |
| 1, 4-Dioxane | 303.15 | 1.0222 | 1.0271 | 1.0985 | 1.0958 |
| Bromo benzene | 303.15 | 1.4815 | 1.4817 | 0.9850 | 1.0201 |
| Ethyl benzene | 303.15 | 0.8645 | 0.8662 | 0.5980 | 0.6020 |

2.2. Apparatus and Procedure

Measurements of the density, ρ , and the kinematic viscosity, γ , of pure liquids and their solutions were carried out using a Pycknometer and Oswald Viscometer and two integrated Pt 100 thermometers. The temperature in the cell was regulated to 0.001K with a proportional temperature controller. The apparatus was first calibrated with triple distilled water. The uncertainties in density measurements were estimated to be $2\cdot 10^{-3} \text{ kg}\cdot\text{m}^{-3}$. Further information about the experimental techniques has been the kinematic viscosities of the pure liquids and their mixtures were measured at (303.15, 308.15, and 313.15) K. The viscometer was filled with liquid mixtures, and its limbs were closed with Teflon caps taking due precaution to reduce evaporation losses. An electronic digital stopwatch with a readability of 0.01 s was used for flow time measurements. Experiments were repeated a minimum of four times for all compositions, and the results were averaged. The caps of the limbs were removed during the measurement of flow times. The measured values of kinematic viscosity, γ , were converted to dynamic viscosity, η , after multiplication by the density. The reproducibility of dynamic viscosity was found to be within 0.003 mPa·s. A thermostatically controlled, well-stirred water bath, whose temperature was controlled to 0.01 K was used for all the measurements, Conductivity measurements were carried out in a jacket containing a conductivity cell of cell constant 1.0 cm^{-1} . Water was circulated in the jacket from thermostat, and the temperature maintained within $\pm 0.01 \text{ K}$, was used for all the measurements. The viscometer with the sample is immersed in a water bath so that it attains the desired temperature. Suction is applied so that liquid is drawn up to mark 'a' through bulb 'd'. The efflux time of the liquid between marks 'a' and 'b' is noted after releasing the vacuum. The viscometer has been calibrated using water. The liquid mixture was charged into the viscometer. After the mixture had attained bath temperature, flow time has been determined. The above steps were continued and reported. The kinematic viscosity of solution γ is given by

$$\gamma = (at / (b/t)) \quad (1)$$

Where γ is the kinematic viscosity, t is the flow time and two constants 'a' and 'b' were obtained by measuring the flow time of benzene and water. The uncertainty for the dynamic viscosity determination is estimated to be $\pm 0.5\%$.

2.1.1. Standard Deviation

Standard deviation has calculated using the relationship.

$$\sigma = \left[\frac{\sum (V_{\text{exp}}^E - V_{\text{cal}}^E)^2}{(N - M)} \right]^{1/2} \quad (2)$$

Where, N-Number of data points

V_{exp}^E -Experimental Excess molar volume

V_{cal}^E - Calculated Excess molar volume

M – Number of coefficients

The calculated values of coefficients along with the standard deviation (σ) are given in Table 8 and Table 9. Interaction parameters and Predicted kinematic viscosities and Excess molar volume of Bromobenzene [2,3] and Ethyl benzene [4,5] and 1, 4 Dioxane mixture at (303.15, 308.15 and 313.15) K are presented in Tables 2,3,4,5,6 and Table 7 respectively.

2.1.2. Nonlinear Model

The binary mixtures 1, 4 Dioxane + Bromo Benzene, 1, 4 Dioxane + Ethyl Benzene. The calculated data of V^E , $\Delta\eta$ were correlated with the composition data by the Redlich-Kister equation. The size ratio of the two molecules should be less than 1.5.

$$V^E = x_1 x_2 \sum a_{i-1} (x_1 - x_2)^{i-1} \quad (3)$$

In case of V^E , excess molar volume is replaced by $\Delta\eta$ in equation 3. The values of coefficients, a_i , were evaluated by using the method of least-squares with all points weighted equally. The coefficients a_1 to a_7 of $\Delta\eta$ and V^E for all temperatures of binary liquid mixtures as shown in Table 8 and Table 9, variations of $\Delta\eta$ and V^E with mole fraction x_1 of 1,4dioxane along with the smoothed $\Delta\eta$ and V^E values calculated by using equation 3 at 303.15K to 313.15K.

3. Results and Discussion

The experimental values of excess molar volume, dynamic viscosities, η , of pure liquids 1, 4-Dioxane, Bromo benzene, and Ethyl benzene at the investigated temperature 303.15K and compared with literature values [2,3,4] are shown in Table 1. The values of V^E are positive and $\Delta\eta$ are negative for all (1, 4-Dioxane +Bromo benzene), (1, 4-Dioxane + Ethyl benzene) systems. The sign of excess volume, of a system depends on the relative magnitude of expansion/contraction on mixing of two liquids. Excess molar volume, V^E , and viscosity deviation, $\Delta\eta$, Predicted Excess molar volume, kinematic viscosities by Redlich-Kister nonlinear model at various temperatures and atmospheric pressure are reported in Tables 2,3,4,5,6 and Table 7, for the 1, 4-Dioxane +Bromo benzene and Ethyl benzene +1, 4 Dioxane

mixtures. The obtained thermo physical data shows high and minimum standard deviations, these are shown in degree precision and it is given Redlitch-Kister constants Table 8 and Table 9.

Table 2. Comparison of Experimental and Prediction of Excess molar volume, kinematic viscosities by Redlitch-Kister nonlinear model for 1, 4 Dioxane + Bromo Benzene at 303.15K

| x_1 | Experimental | | | | Prediction | | | |
|--------|------------------------------------|--------------------------------|---------------------------------------|-------------------------------------|----------------------------------------|--------------|--------------------------------|--------------|
| | $\rho/\text{g}\cdot\text{cm}^{-3}$ | $\eta/\text{mPa}\cdot\text{s}$ | $V^E/\text{cm}^3\cdot\text{mol}^{-1}$ | $\gamma_{\text{expt}}(\text{C.S.})$ | $V^E(\text{cm}^3\cdot\text{mol}^{-1})$ | ΔV^E | $\eta/\text{mPa}\cdot\text{s}$ | $\Delta\eta$ |
| 0.0000 | 1.4817 | 1.0201 | 0.0000 | 0.6863 | 0.0000 | 0.0000 | 1.0201 | 0.0000 |
| 0.1047 | 1.4432 | 1.0255 | 0.7354 | 0.7106 | 0.7125 | 0.0229 | 1.0182 | -0.0073 |
| 0.2083 | 1.3962 | 1.0302 | 1.1127 | 0.7379 | 0.8569 | 0.2558 | 1.0202 | -0.0100 |
| 0.3109 | 1.3468 | 1.0333 | 1.5952 | 0.7672 | 1.4569 | 0.1383 | 1.0200 | -0.0133 |
| 0.4124 | 1.2965 | 1.0333 | 2.0647 | 0.7919 | 1.7569 | 0.3078 | 1.0123 | -0.0210 |
| 0.5128 | 1.2496 | 1.0355 | 2.1888 | 0.8229 | 1.9895 | 0.1993 | 1.0095 | -0.0260 |
| 0.6122 | 1.1999 | 1.0450 | 2.4288 | 0.8655 | 2.3526 | 0.0762 | 1.0213 | -0.0237 |
| 0.7106 | 1.1578 | 1.0569 | 1.9581 | 0.9129 | 1.9465 | 0.0116 | 1.0386 | -0.0183 |
| 0.8080 | 1.1125 | 1.0688 | 1.6402 | 0.9607 | 1.6301 | 0.0101 | 1.0543 | -0.0145 |
| 0.9045 | 1.0698 | 1.0800 | 1.1176 | 1.0095 | 1.1134 | 0.0042 | 1.0712 | -0.0088 |
| 1.0000 | 1.0271 | 1.0958 | 0.0000 | 1.0669 | 0.0000 | 0.0000 | 1.0958 | 0.0000 |

Table 3. Comparison of Experimental and Prediction of Excess molar volume, kinematic viscosities by Redlitch-Kister nonlinear model for 1, 4 Dioxane + Bromo Benzene at 308.15K

| x_1 | Experimental | | | | Prediction | | | |
|--------|------------------------------------|--------------------------------|---------------------------------------|-------------------------------------|----------------------------------------|--------------|--------------------------------|--------------|
| | $\rho/\text{g}\cdot\text{cm}^{-3}$ | $\eta/\text{mPa}\cdot\text{s}$ | $V^E/\text{cm}^3\cdot\text{mol}^{-1}$ | $\gamma_{\text{expt}}(\text{C.S.})$ | $V^E(\text{cm}^3\cdot\text{mol}^{-1})$ | ΔV^E | $\eta/\text{mPa}\cdot\text{s}$ | $\Delta\eta$ |
| 0.0000 | 1.4682 | 0.9815 | 0.0000 | 0.6685 | 0.0000 | 0.0000 | 0.9815 | 0.0000 |
| 0.1047 | 1.4267 | 0.9785 | 0.5469 | 0.6858 | 0.5407 | 0.0062 | 0.9844 | -0.0059 |
| 0.2083 | 1.3819 | 0.9795 | 0.8984 | 0.7088 | 0.8394 | 0.0590 | 0.9874 | -0.0079 |
| 0.3109 | 1.3356 | 0.9886 | 1.2546 | 0.7335 | 1.1785 | 0.0761 | 0.9985 | -0.0099 |
| 0.4124 | 1.2826 | 0.9875 | 1.7914 | 0.7562 | 1.6934 | 0.0980 | 1.0031 | -0.0156 |
| 0.5128 | 1.2373 | 0.9735 | 2.0053 | 0.7808 | 1.9620 | 0.0433 | 0.9932 | -0.0197 |
| 0.6122 | 1.1899 | 0.9555 | 1.9880 | 0.8187 | 1.8028 | 0.1852 | 0.9739 | -0.0184 |
| 0.7106 | 1.1499 | 0.9589 | 1.6459 | 0.8618 | 1.5106 | 0.1353 | 0.9730 | -0.0141 |
| 0.8080 | 1.1036 | 0.9705 | 1.3838 | 0.9011 | 1.2973 | 0.0865 | 0.9810 | -0.0105 |
| 0.9045 | 1.0596 | 0.9717 | 0.7805 | 0.9445 | 0.7711 | 0.0094 | 0.9778 | -0.0061 |
| 1.0000 | 1.0169 | 1.0094 | 0.0000 | 0.9927 | 0.0000 | 0.0000 | 1.0094 | 0.0000 |

Table 4. Comparison of Experimental and Prediction of Excess molar volume, kinematic viscosities by Redlitch-Kister nonlinear model for 1, 4 Dioxane + Bromo Benzene at 313.15K

| x_1 | Experimental | | | | Prediction | | | |
|--------|------------------------------------|--------------------------------|---------------------------------------|-------------------------------------|----------------------------------------|--------------|--------------------------------|--------------|
| | $\rho/\text{g}\cdot\text{cm}^{-3}$ | $\eta/\text{mPa}\cdot\text{s}$ | $V^E/\text{cm}^3\cdot\text{mol}^{-1}$ | $\gamma_{\text{expt}}(\text{C.S.})$ | $V^E(\text{cm}^3\cdot\text{mol}^{-1})$ | ΔV^E | $\eta/\text{mPa}\cdot\text{s}$ | $\Delta\eta$ |
| 0.0000 | 1.4549 | 0.9550 | 0.0000 | 0.6564 | 0.0000 | 0.0000 | 0.9550 | 0.0000 |
| 0.1047 | 1.4129 | 0.9429 | 0.3930 | 0.6700 | 0.2986 | 0.0944 | 0.9496 | -0.0067 |
| 0.2083 | 1.3698 | 0.9489 | 0.6855 | 0.6980 | 0.5167 | 0.1688 | 0.9712 | -0.0223 |
| 0.3109 | 1.3256 | 0.9480 | 1.1992 | 0.7182 | 1.0909 | 0.1083 | 0.9982 | -0.0502 |
| 0.4124 | 1.2775 | 0.9467 | 1.3704 | 0.7411 | 1.1593 | 0.2111 | 1.0243 | -0.0776 |
| 0.5128 | 1.2308 | 0.9370 | 1.6700 | 0.7613 | 1.4501 | 0.2199 | 1.0280 | -0.0910 |
| 0.6122 | 1.1873 | 0.9162 | 1.7245 | 0.7746 | 1.3576 | 0.3669 | 1.0148 | -0.0986 |
| 0.7106 | 1.1467 | 0.9011 | 1.1760 | 0.7958 | 1.1098 | 0.0662 | 1.0153 | -0.1142 |
| 0.8080 | 1.1026 | 0.9203 | 0.8960 | 0.8457 | 0.8637 | 0.0323 | 1.0411 | -0.1208 |
| 0.9045 | 1.0568 | 0.9145 | 0.6064 | 0.8757 | 0.5359 | 0.0705 | 0.9882 | -0.0737 |
| 1.0000 | 1.0128 | 0.9447 | 0.0000 | 0.9327 | 0.0000 | 0.0000 | 0.9447 | 0.0000 |

Table 5. Comparison of Experimental and Prediction of Excess molar volume, kinematic viscosities by Redlitch-Kister nonlinear model for 1, 4 Dioxane + Ethyl Benzene at 303.15K

| x_1 | Experimental | | | | Prediction | | | |
|--------|------------------------------------|--------------------------------|---------------------------------------|-------------------------------------|----------------------------------------|--------------|--------------------------------|--------------|
| | $\rho/\text{g}\cdot\text{cm}^{-3}$ | $\eta/\text{mPa}\cdot\text{s}$ | $V^E/\text{cm}^3\cdot\text{mol}^{-1}$ | $\gamma_{\text{expt}}(\text{C.S.})$ | $V^E(\text{cm}^3\cdot\text{mol}^{-1})$ | ΔV^E | $\eta/\text{mPa}\cdot\text{s}$ | $\Delta\eta$ |
| 0.0000 | 0.8662 | 0.6020 | 0.0000 | 0.7042 | 0.0000 | 0.0000 | 0.6020 | 0.0000 |
| 0.1047 | 0.9068 | 0.6514 | 0.7737 | 0.7193 | 0.7495 | 0.0242 | 0.6854 | -0.0340 |
| 0.2083 | 0.9135 | 0.6663 | 1.1728 | 0.7298 | 1.1297 | 0.0431 | 0.7287 | -0.0624 |
| 0.3109 | 0.9218 | 0.6934 | 1.4122 | 0.7522 | 1.3095 | 0.1027 | 0.7792 | -0.0858 |
| 0.4124 | 0.9301 | 0.7161 | 1.6919 | 0.7689 | 1.5621 | 0.1298 | 0.8284 | -0.1123 |
| 0.5128 | 0.9399 | 0.7489 | 1.8462 | 0.7924 | 1.6591 | 0.1871 | 0.8740 | -0.1251 |
| 0.6122 | 0.9534 | 0.7925 | 1.6595 | 0.8302 | 1.5415 | 0.1180 | 0.9149 | -0.1224 |
| 0.7106 | 0.9687 | 0.8390 | 1.3748 | 0.8677 | 1.3663 | 0.0085 | 0.9593 | -0.1203 |
| 0.8080 | 0.9876 | 0.8986 | 0.8473 | 0.9236 | 0.8404 | 0.0069 | 1.0137 | -0.1151 |
| 0.9045 | 1.0069 | 0.9711 | 0.4005 | 0.9722 | 0.3965 | 0.0040 | 1.0404 | -0.0693 |
| 1.0000 | 1.0271 | 1.0958 | 0.0000 | 1.0669 | 0.0000 | 0.0000 | 1.0958 | 0.0000 |

Table 6. Comparison of Experimental and Prediction of Excess molar volume, kinematic viscosities by Redlitch-Kister nonlinear model for 1, 4 Dioxane + Ethyl Benzene at 308.15K

| x_1 | Experimental | | | | Prediction | | | |
|--------|------------------------------------|--------------------------------|---------------------------------------|-----------------------------|----------------------------------------|--------------|--------------------------------|--------------|
| | $\rho/\text{g}\cdot\text{cm}^{-3}$ | $\eta/\text{mPa}\cdot\text{s}$ | $V^E/\text{cm}^3\cdot\text{mol}^{-1}$ | $\gamma_{\text{expt}}(C.S)$ | $V^E(\text{cm}^3\cdot\text{mol}^{-1})$ | ΔV^E | $\eta/\text{mPa}\cdot\text{s}$ | $\Delta\eta$ |
| 0.0000 | 0.8595 | 0.5893 | 0.0000 | 0.6855 | 0.0000 | 0.0000 | 0.5893 | 0.0000 |
| 0.1047 | 0.8948 | 0.6220 | 0.6049 | 0.6951 | 0.5886 | 0.0163 | 0.6531 | -0.0311 |
| 0.2083 | 0.9030 | 0.6399 | 0.8638 | 0.7086 | 0.8166 | 0.0472 | 0.6897 | -0.0498 |
| 0.3109 | 0.9118 | 0.6665 | 1.0935 | 0.7310 | 1.0421 | 0.0514 | 0.7336 | -0.0671 |
| 0.4124 | 0.9207 | 0.6844 | 1.3569 | 0.7433 | 1.3240 | 0.0329 | 0.7782 | -0.0938 |
| 0.5128 | 0.9310 | 0.7073 | 1.5074 | 0.7597 | 1.3972 | 0.1102 | 0.8165 | -0.1092 |
| 0.6122 | 0.9445 | 0.7421 | 1.3707 | 0.7857 | 1.3197 | 0.0510 | 0.8504 | -0.1083 |
| 0.7106 | 0.9602 | 0.7874 | 1.0924 | 0.8200 | 1.0521 | 0.0403 | 0.8958 | -0.1084 |
| 0.8080 | 0.9786 | 0.8440 | 0.6535 | 0.8625 | 0.6520 | 0.0015 | 0.9523 | -0.1083 |
| 0.9045 | 0.9976 | 0.8858 | 0.2830 | 0.8879 | 0.2827 | 0.0003 | 0.9539 | -0.0681 |
| 1.0000 | 1.0169 | 1.0095 | 0.0000 | 0.9927 | 0.0000 | 0.0000 | 1.0095 | 0.0000 |

Table 7. Comparison of Experimental and Prediction of Excess molar volume, kinematic viscosities by Redlitch-Kister nonlinear model for 1, 4 Dioxane + Ethyl Benzene at 313.15K

| x_1 | Experimental | | | | Prediction | | | |
|--------|------------------------------------|--------------------------------|---------------------------------------|-----------------------------|----------------------------------------|--------------|--------------------------------|--------------|
| | $\rho/\text{g}\cdot\text{cm}^{-3}$ | $\eta/\text{mPa}\cdot\text{s}$ | $V^E/\text{cm}^3\cdot\text{mol}^{-1}$ | $\gamma_{\text{expt}}(C.S)$ | $V^E(\text{cm}^3\cdot\text{mol}^{-1})$ | ΔV^E | $\eta/\text{mPa}\cdot\text{s}$ | $\Delta\eta$ |
| 0.0000 | 0.8519 | 0.5699 | 0.0000 | 0.6690 | 0.0000 | 0.0000 | 0.5699 | 0.0000 |
| 0.1047 | 0.8615 | 0.5957 | 0.3975 | 0.6812 | 0.0022 | 0.3953 | 0.6099 | -0.0142 |
| 0.2083 | 0.8725 | 0.6161 | 0.6663 | 0.6910 | 0.5167 | 0.1496 | 0.6462 | -0.0301 |
| 0.3109 | 0.8845 | 0.6379 | 0.9803 | 0.7100 | 0.7409 | 0.2394 | 0.6859 | -0.0480 |
| 0.4124 | 0.8974 | 0.6600 | 1.0629 | 0.7266 | 0.8593 | 0.2036 | 0.7278 | -0.0678 |
| 0.5128 | 0.9120 | 0.6808 | 1.1312 | 0.7411 | 1.0501 | 0.0811 | 0.7622 | -0.0814 |
| 0.6122 | 0.9300 | 0.7068 | 0.9261 | 0.7607 | 0.8576 | 0.0685 | 0.7962 | -0.0894 |
| 0.7106 | 0.9498 | 0.7379 | 0.6624 | 0.7885 | 0.6098 | 0.0526 | 0.8353 | -0.0974 |
| 0.8080 | 0.9712 | 0.7814 | 0.3894 | 0.8099 | 0.3570 | 0.0324 | 0.8756 | -0.0942 |
| 0.9045 | 0.9935 | 0.8539 | 0.1881 | 0.8455 | 0.1606 | 0.0275 | 0.9077 | -0.0538 |
| 1.0000 | 1.0128 | 0.9446 | 0.0000 | 0.9327 | 0.0000 | 0.0000 | 0.9446 | 0.0000 |

Table 8. Parameters of studied Redlitch-Kister nonlinear model, constants and standard deviations (σ) of 1, 4 Dioxane + Bromo Benzene, at 303.15, 308.15 and 313.15 K

| Redlich Kister Constants | (Excess Volume) | | | (Viscosity Deviation) | | |
|--------------------------|-----------------|-----------|-----------|-----------------------|-----------|-----------|
| | 303.15(K) | 308.15(K) | 313.15(K) | 303.15(K) | 308.15(K) | 313.15(K) |
| a_1 | -56.5 | -44.51 | -87.369 | 0.8987 | 0.498 | 1.8420 |
| a_2 | -27.65 | -5.694 | -102.9 | 0.0305 | -0.051 | 1.8177 |
| a_3 | 66.61 | 53.25 | 76.667 | -0.9624 | -0.64 | -1.5655 |
| a_4 | 26.96 | 3.72 | 98.355 | 0.2016 | 0.096 | -1.6702 |
| a_5 | -15.73 | -16.53 | -3.677 | 0.3993 | 0.221 | 0.0816 |
| a_6 | 0.76 | 1.983 | 5.0706 | 0.232 | -0.044 | 0.1671 |
| a_7 | 5.655 | 7.813 | 15.481 | -0.336 | -0.078 | -0.360 |
| σ | 0.2633 | 0.1504 | 0.0991 | 0.0652 | 0.0016 | 0.0108 |

Table 9. Parameters of studied Redlitch-Kister nonlinear model, constants and standard deviations (σ) of 1, 4 Dioxane + Ethyl Benzene, at 303.15, 308.15 and 313.15 K

| Redlich Kister Constants | (Excess Volume) | | | (Viscosity Deviation) | | |
|--------------------------|-----------------|-----------|-----------|-----------------------|-----------|-----------|
| | 303.15(K) | 308.15(K) | 313.15(K) | 303.15(K) | 308.15(K) | 313.15(K) |
| a_1 | 9.411 | -23.903 | -87.369 | 4.434 | 3.841 | 3.451 |
| a_2 | 11.967 | 11.13 | -102.9 | 2.343 | 1.527 | 1.800 |
| a_3 | 32.111 | 27.826 | 76.667 | -5.013 | -4.342 | -4.045 |
| a_4 | -13.888 | -13.373 | 98.355 | 2.612 | -1.654 | -2.032 |
| a_5 | -10.09 | -9.978 | -3.677 | 0.981 | 0.811 | 0.778 |
| a_6 | 1.9045 | 2.2156 | 5.0706 | 0.255 | 0.116 | 0.224 |
| a_7 | 7.3992 | 6.0627 | 15.481 | -0.408 | -0.314 | -0.187 |
| σ | 0.6825 | 0.6150 | 0.5547 | 0.020 | 0.015 | 0.012 |

The excess molar volumes, V^E , dynamic viscosity, η , and molar refraction changes of mixing were calculated from experimental values using the following expressions.

$$V^E = V_M - \sum_{i=1}^n X_i V_i \quad (4)$$

Where V_M is the molar volume of the mixture, η is the dynamic viscosity, and V_i is Molar volume.

The variation of excess volumes with the mole fraction of Bromobenzene and Ethylebenzene with 1, 4 Dioxane at (303.15, 308.15 and 313.15) K are represented in Figure 1 and Figure 2.

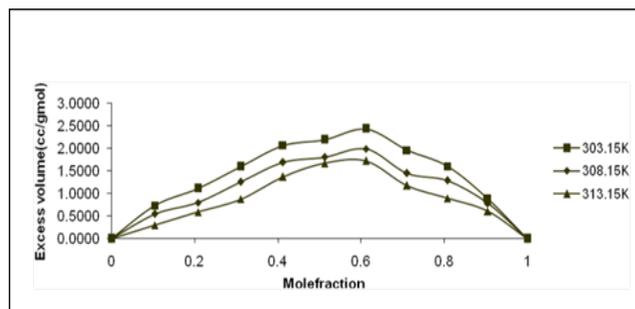


Figure 1. Excess molar volume (V^E) for 1, 4 Dioxane + Bromo Benzene at 303.15, 308.15 and 313.15 K

The sign of excess volume of a system depends on the relative magnitude of expansion/contraction on mixing of two liquids. If the factors causing expansion dominate the contraction factors, the (V^E) becomes positive.

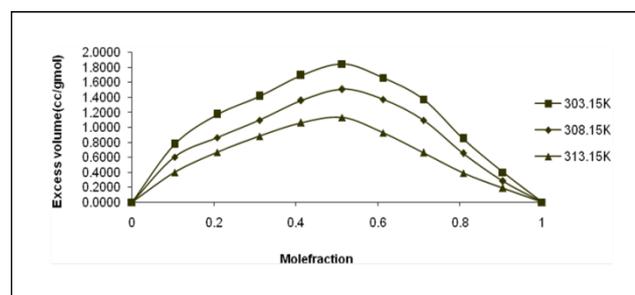


Figure 2. Excess molar volume (V^E) for 1, 4 Dioxane + Ethyl Benzene at 303.15, 308.15 and 313.15 K

On the other hand if the contraction factors dominate the expansion factors, then V^E become negative. The factors that are responsible for expansion in volume are as follows, i. Loss of dipolar association, ii. The geometry of molecular structure, which does not allow fitting of one component into other component, iii. Steric hindrance opposes proximity of the constituent molecules. The negative V^E values arise due to dominance of the following factors. i. Chemical interaction between constituent chemicals. ii. Accommodation of molecules of one component into the interstitials of the molecules of the other component [8,9]. iii. Geometry of the molecular structure that favors fitting of the component molecules with each other [9,10]. The negative V^E values in the mixtures under study indicate that interactions between molecules of the mixtures are stronger than interactions between molecules in the pure liquids and that associative force dominate the behaviour of the solution.

$$\Delta\eta = \eta - \sum_{i=1}^n x_i \eta_i \quad (5)$$

Where ($\Delta\eta$) is the viscosity deviation of the mixture, η is the dynamic viscosity.

The results of variation in viscosity deviations of binary systems consisting of Bromobenzene and Ethylebenzene with 1, 4 Dioxane at temperatures of 303.15K, 308.15K, and 313.15K are represented in Figure 3 and Figure 4.

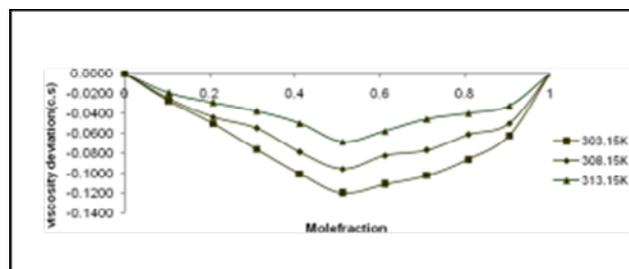


Figure 3. Deviation in viscosity ($\Delta\eta$) for 1,4 Dioxane + Bromo Benzene at 303.15, 308.15 and 313.15 K

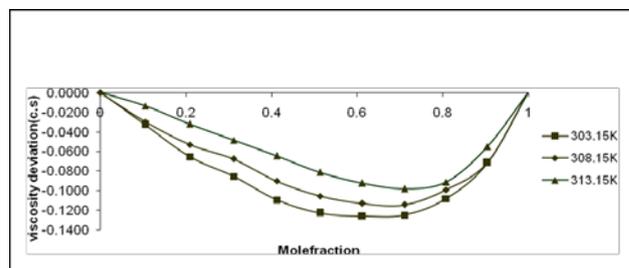


Figure 4. Deviation in viscosity ($\Delta\eta$) for 1,4Dioxane + Ethyl Benzene at 303.15, 308.15 and 313.15 K

This result shows negative deviations [6,7,11] over the entire range of mole fraction. The viscosity of the mixture strongly depends on the entropy of mixture, which is related with liquid's structure and enthalpy. It will consequently with molecular interactions between the components of the mixtures. Therefore the viscosity deviation depends on molecular interactions as well as on the size and shape of the molecules.

4. Conclusion

In the present study, Viscosities (η) and Excess molar volume (V^E), for the binary liquid mixture of 1, 4 Dioxane + Bromo benzene + Ethyl benzene system was found out as a function of mole fraction at atmospheric pressure and at temperatures of 303.15K, 308.15K, and 313.15K. The excess values of the mixtures show a systematic change with increasing temperature. With an increase in temperature the intermolecular interactions between molecules become weak. 1, 4 Dioxane is repulse towards the Bromine group in bromobenzene and it forms dipole-dipole bond. In this case, the force between unlike molecules is lesser than the force between like molecules in mixtures. It can be concluded that the positive excess molar volumes and negative deviations viscosity due to weak molecular interactions in mixtures. Viscosity and density of the binary mixture and the Redlich-Kister model is very well suited for correlating Kinematic viscosity and Excess molar volumes of the binary mixture with minimum standard deviation in present study and it is far superior to the other predictive models.

References

- [1] Martin Contreras S. 2001 Densities and Viscosities of Binary Mixtures of 1, 4-Dioxane with 1-Propanol and 2-Propanol at (25, 30, 35, and 40) °C *J. Chem. Eng. Data*, 46, 1149-1152.
- [2] R.Ramesh.,A.Hisyam.,K.Ramesh.,Measurement and Prediction of Thermo Physical Properties of Binary Liquid Mixtures at Various Temperatures Using Mc Allister Model, *IJES.*, 3, 68-74 (2014).
- [3] JouybanA.,KhoubnasabjafariM.,Vaezgharamaleki., Z.,Fekari Z. and Jr.Acree, W.E., Calculation of the viscosity of binary liquid mixture at various temperatures using Jouyban - Acree model, *Chemical and Pharmaceutical Bulletin.*, 53, 519-523 (2005).
- [4] Redlich O. and Kister A.T., Algebraic representation of thermodynamic properties and the classification of solutions, *Ind. Eng. Chem*, 40, 345-349 (1948).
- [5] Vadamar R. Mani D. and Balakrishnan, Ultrasonic Study of Binary Liquid Mixtures of Methyl Methacrylate with Alcohols, *Res.J.Chem.Sci.*, 1(9), 79-82 (2011).
- [6] S. Senthil Raja and T. R Kubendran, 2004. Viscosities and Densities of Binary Mixtures of 1, 4 - Dioxane, Carbon Tetrachloride, and Butanol at 303.15K, 308.15K, and 313.15K *J. Chem. Eng. Data*, 49, 421-425.
- [7] Baskaran. R. and Kubendran. T.R, 2007. Intermolecular Interactions in Binary Liquid Mixtures, Of Anisaldehyde with Nitrobenzene and Ethyl Benzene by Ultrasonic Measurements at (303.15, 313.15 and 313.15) K, *Chemical Physics Research Journal*, 2: 1-14.
- [8] Fabio Comelli, Romolo Francesconi, Adriana Bigi, and Katia Rubini, 2006. Excess Molar Enthalpies, Molar Heat Capacities, Densities, Viscosities, and Refractive Indices of Dimethyl Sulfoxide + Esters of Carbonic Acid at 308.15 K and Atmospheric Pressure *J. Chem. Eng. Data*, 51, 665-670.
- [9] Francesconi, R.; Bigi, A.; Rubini, K.; Comelli, F. 2005 Excess enthalpies, heat Capacities, densities, viscosities, and refractive indices of dimethyl sulfoxide + three aryl alcohols at 308.14 K and atmospheric pressure. *J. Chem. Eng. Data*, 50, 1932-1937.
- [10] Hiannie, D.; Suryadi, I. 2005 Density and viscosity of several aldehydes fragrance compounds in their binary mixtures with ethanol at 298.15, 308.15 and 318.15 K. *J. Chem. Eng. Data*, 50, 2003-2007.
- [11] S. Senthil Raja and T. R Kubendran, 2004. Viscosities and Densities of Binary Mixtures of 1, 4 Dioxane, Carbon Tetrachloride, and Butanol at 303.15K, 308.15K, and 313.15K *J. Chem. Eng. Data*, 49, 421-425.