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# Viscosity, Density, and Refractive Index of Some (Ester + Hydrocarbon) Binary Mixtures at 303.15 K and 313.15 K

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The viscosity, density, and refractive index of binary mixtures of ethyl formate or ethyl benzoate with *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene were determined at 303.15 K and 313.15 K and atmospheric pressure for the whole composition range. From the experimental measurements, the deviations in viscosity, $\Delta\eta$, were correlated accurately with the Redlich−Kister polynomial equation. The deviations in molar refraction, $\Delta R$, were calculated from the Lorentz−Lorentz equation. The experimental viscosities were fitted to an empirical equation proposed by Frenkel. It was observed that the equation predicts the mixture viscosities reasonably well at both temperatures and the agreement between the experimental and calculated values is satisfactory.

## Introduction

A detailed study of the thermodynamic, transport, and dielectric properties of fluids and fluid mixtures is important not only for the solution problems concerning vapor−liquid equilibria, heat transfer, fluidity, and so forth but also for the development of our understanding of molecular motions and interactions in such systems.[1,2] Recently, interest in the study of liquid mixtures containing esters as one of the components[3−9] has increased. These studies are of great significance because one can get information regarding structural changes that occur in the pure ester because of the mixing, and they are also useful from the viewpoint of building up a valid theory and testing the existing ones. Viscosity is an important bulk property that provides a measure of the internal friction of a fluid and is closely related to self-association in liquids. Therefore, viscosity results of liquid mixtures are essential in chemical engineering for the determination of flow in pipelines, heat transfer, and so forth. A literature survey reveals that very few attempts[10−16] have been made to study the viscosity of liquid mixtures consisting of a variety of esters in different solvents. Esters possess high dipole moments but behave like normal liquids; this behavior is quite different from that of alcohols, ketones, and acids. Therefore, it is of interest to study the viscosities of esters and their binary mixtures. In continuation of our previous work,[17,18] we report in this paper the measurements of viscosities, densities, and refractive indexes of binary liquid mixtures of (ethyl formate + *o*-xylene, *m*-xylene, *p*-xylene, or ethylbenzene) and (ethyl benzoate + *o*-xylene, *m*-xylene, *p*-xylene, or ethylbenzene) at the temperatures (303.15 and 313.15) K and atmospheric pressure. The deviations in viscosity and the deviations in molar refraction were then calculated. The deviations in viscosity were correlated by a polynomial expression.

**Table 1. Comparison of Experimental Densities ($\rho$), Dynamic Viscosities ($\eta$), and Refractive Indexes ($n_D$) of Pure Liquids with Literature Values**

| | | $\rho$/kg·m$^{-3}$ | | $\eta$/mPa·s | | $n_D$ | |
|---|---|---|---|---|---|---|---|
| liquid | *T*/K | exptl | lit[a] | exptl | lit[a] | exptl | lit[b] |
| ethyl formate | 303.15 | 908.1 | 908.5[b] | 0.366 | 0.358 | 1.3552 | 1.3552 |
| | 313.15 | 894.9 | | 0.339 | | 1.3549 | |
| ethyl benzoate | 303.15 | 1037.4 | 1037.2 | 1.748 | 1.751 | 1.5009 | 1.5015 |
| | 313.15 | 1028.5 | | 1.438 | | 1.4997 | |
| *o*-xylene | 303.15 | 870.8 | 871.7 | 0.695 | 0.693[c] | 1.5001 | 1.5002[c] |
| | 313.15 | 863.3 | | 0.621 | | 1.4981 | |
| *m*-xylene | 303.15 | 855.3 | 855.8 | 0.557 | | 1.4920 | 1.4921 |
| | 313.15 | 847.1 | | 0.508 | | 1.4901 | |
| *p*-xylene | 303.15 | 851.9 | 852.2 | 0.566 | 0.566 | 1.4911 | 1.4906[c] |
| | 313.15 | 844.0 | | 0.517 | | 1.4902 | |
| ethylbenzene | 303.15 | 857.6 | 858.1[b] | 0.597 | 0.590[c] | 1.4910 | 1.4906 |
| | 313.15 | 849.2 | | 0.538 | | 1.4891 | |

[a] Reference 19. [b] Extrapolated values from ref 19. [c] Reference 20.

## Experimental Section

Chemicals *o*-xylene, *m*-xylene, *p*-xylene, all analytical grade (BDH), were purified as per the standard procedure given by Riddick et al.[19] Ethyl benzene, ethyl formate, and ethyl benzoate, all (Fluka, AG) with a reported purity of >99%, were used without further treatment. All of the chemicals were distilled before use, and the purity of these samples was tested by measuring their densities, viscosities, and refractive indexes at 303.15 K. Table 1 lists the densities, viscosities, and refractive indexes of the pure components, together with the literature values,[19,20] at 303.15 K.

***Apparatus and Procedure.*** Liquid mixtures were prepared by mass using a Mettler balance with an accuracy of ±0.02 mg. The uncertainty of the mole fraction was estimated to be lower than $\pm 4 \times 10^{-4}$. To prevent the samples from preferential evaporation, the mixtures were prepared by transferring aliquots via syringe into suitably

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**Table 2. Densities ($\rho$), Dynamic Viscosities ($\eta$), Deviations in Viscosity ($\Delta\eta$), Refractive Indexes ($n_D$), and Deviations in Refractive Index ($\Delta R$) for Various Binary Mixtures**

| $X_1$ | $\rho$ / kg·m$^{-3}$ | $\eta$ / mPa·s exptl | $\eta$ / mPa·s eq 3 | $\Delta\eta$ / mPa·s | $n_D$ | ΔR / cm$^3$mo1$^{-1}$ | $X_1$ | $\rho$ / kg·m$^{-3}$ | $\eta$ / mPa·s exptl | $\eta$ / mPa·s eq 3 | $\Delta\eta$ / mPa·s | $n_D$ | ΔR / cm$^3$mo1$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ethyl Formate (1) + *o*-Xylene (2) at 303.15 K | | | | | | | | | | | | | |
| 0.1467 | 872.7 | 0.630 | 0.632 | −0.017 | 1.4906 | 5.862 | 0.6940 | 891.2 | 0.444 | 0.444 | −0.023 | 1.4347 | 12.823 |
| 0.2667 | 877.4 | 0.586 | 0.585 | −0.021 | 1.4873 | 11.704 | 0.7791 | 896.7 | 0.420 | 0.421 | −0.018 | 1.4072 | 10.220 |
| 0.3779 | 880.0 | 0.544 | 0.544 | −0.027 | 1.4786 | 12.418 | 0.8563 | 901.2 | 0.400 | 0.401 | −0.013 | 1.3981 | 7.893 |
| 0.4984 | 882.6 | 0.502 | 0.504 | −0.029 | 1.4721 | 14.245 | 0.9337 | 903.7 | 0.378 | 0.382 | −0.009 | 1.3729 | 3.516 |
| 0.5936 | 886.9 | 0.471 | 0.474 | −0.028 | 1.4631 | 14.456 | | | | | | | |
| Ethyl Formate (1) + *o*-Xylene (2) at 313.15 K | | | | | | | | | | | | | |
| 0.1467 | 864.6 | 0.558 | 0.556 | −0.021 | 1.4896 | 6.384 | 0.6940 | 881.6 | 0.402 | 0.405 | −0.023 | 1.4216 | 12.267 |
| 0.2667 | 868.5 | 0.521 | 0.525 | −0.025 | 1.4819 | 9.790 | 0.7791 | 885.9 | 0.382 | 0.385 | −0.019 | 1.4061 | 10.291 |
| 0.3779 | 871.9 | 0.487 | 0.490 | −0.027 | 1.4735 | 12.395 | 0.8563 | 889.6 | 0.366 | 0.368 | −0.014 | 1.3969 | 7.946 |
| 0.4984 | 873.7 | 0.452 | 0.456 | −0.028 | 1.4671 | 14.286 | 0.9337 | 891.1 | 0.359 | 0.352 | −0.001 | 1.3701 | 3.922 |
| 0.5936 | 876.9 | 0.430 | 0.430 | −0.025 | 1.4612 | 14.598 | | | | | | | |
| Ethyl Formate (1) + *m*-Xylene (2) at 303.15 K | | | | | | | | | | | | | |
| 0.1348 | 858.3 | 0.524 | 0.526 | −0.008 | 1.4892 | 5.778 | 0.6923 | 882.8 | 0.414 | 0.415 | −0.011 | 1.4265 | 12.598 |
| 0.2728 | 863.3 | 0.494 | 0.496 | −0.011 | 1.4695 | 9.460 | 0.7867 | 888.4 | 0.398 | 0.399 | −0.009 | 1.4055 | 10.231 |
| 0.3968 | 868.7 | 0.467 | 0.470 | −0.014 | 1.4561 | 11.951 | 0.8591 | 895.0 | 0.386 | 0.388 | −0.007 | 1.3875 | 7.487 |
| 0.4988 | 873.1 | 0.449 | 0.450 | −0.013 | 1.4391 | 12.761 | 0.9379 | 900.1 | 0.373 | 0.375 | −0.005 | 1.3856 | 4.581 |
| 0.6032 | 877.7 | 0.430 | 0.431 | −0.012 | 1.4288 | 12.981 | | | | | | | |
| Ethyl Formate (1) + *m*-Xylene (2) at 313.15 K | | | | | | | | | | | | | |
| 0.1348 | 849.8 | 0.479 | 0.480 | −0.006 | 1.4820 | 5.457 | 0.6923 | 874.3 | 0.384 | 0.383 | −0.007 | 1.4253 | 12.642 |
| 0.2728 | 854.4 | 0.453 | 0.454 | −0.009 | 1.4679 | 9.589 | 0.7867 | 880.1 | 0.369 | 0.369 | −0.006 | 1.4043 | 10.219 |
| 0.3968 | 859.5 | 0.431 | 0.431 | −0.010 | 1.4578 | 12.256 | 0.8591 | 884.1 | 0.357 | 0.358 | −0.006 | 1.3850 | 7.445 |
| 0.4988 | 864.3 | 0.412 | 0.414 | −0.012 | 1.4380 | 12.872 | 0.9379 | 889.7 | 0.347 | 0.347 | −0.002 | 1.3841 | 4.465 |
| 0.6032 | 869.2 | 0.397 | 0.397 | −0.009 | 1.4276 | 13.070 | | | | | | | |
| Ethyl Formate (1) + *p*-Xylene (2) at 303.15 K | | | | | | | | | | | | | |
| 0.1658 | 857.7 | 0.523 | 0.525 | −0.010 | 1.4785 | 6.552 | 0.6916 | 883.4 | 0.418 | 0.417 | −0.010 | 1.4239 | 14.827 |
| 0.2572 | 861.1 | 0.503 | 0.505 | −0.011 | 1.4746 | 9.461 | 0.7854 | 889.6 | 0.403 | 0.401 | −0.005 | 1.1421 | 10.542 |
| 0.4068 | 868.2 | 0.472 | 0.472 | −0.013 | 1.4671 | 12.882 | 0.8588 | 896.0 | 0.390 | 0.388 | −0.004 | 1.3901 | 8.181 |
| 0.5039 | 871.6 | 0.452 | 0.453 | −0.013 | 1.4532 | 13.674 | 0.9381 | 902.9 | 0.375 | 0.376 | −0.003 | 1.3711 | 3.976 |
| 0.6037 | 878.8 | 0.434 | 0.433 | −0.011 | 1.4510 | 14.154 | | | | | | | |
| Ethyl Formate (1) + *p*-Xylene (2) at 313.15 K | | | | | | | | | | | | | |
| 0.1658 | 849.0 | 0.477 | 0.478 | −0.010 | 1.4779 | 6.414 | 0.6916 | 873.5 | 0.380 | 0.381 | −0.014 | 1.4201 | 12.376 |
| 0.2572 | 851.7 | 0.451 | 0.450 | −0.019 | 1.4732 | 9.405 | 0.7854 | 877.8 | 0.371 | 0.368 | −0.006 | 1.4091 | 10.560 |
| 0.4068 | 858.8 | 0.424 | 0.429 | −0.021 | 1.4611 | 12.598 | 0.8588 | 884.7 | 0.360 | 0.357 | −0.004 | 1.3891 | 8.077 |
| 0.5039 | 861.8 | 0.407 | 0.412 | −0.020 | 1.4499 | 13.596 | 0.9381 | 891.0 | 0.348 | 0.347 | −0.002 | 1.3689 | 3.736 |
| 0.6037 | 868.8 | 0.393 | 0.395 | −0.016 | 1.4491 | 14.157 | | | | | | | |
| Ethyl Formate (1) + Ethylbenzene (2) at 303.15 K | | | | | | | | | | | | | |
| 0.1478 | 862.2 | 0.558 | 0.557 | −0.005 | 1.4809 | 5.767 | 0.6925 | 886.6 | 0.430 | 0.427 | −0.007 | 1.4157 | 11.960 |
| 0.2728 | 869.9 | 0.527 | 0.525 | −0.007 | 1.4691 | 9.301 | 0.7768 | 891.0 | 0.413 | 0.410 | −0.005 | 1.4058 | 10.371 |
| 0.3884 | 871.2 | 0.499 | 0.496 | −0.008 | 1.4568 | 11.796 | 0.8510 | 896.6 | 0.397 | 0.395 | −0.003 | 1.3938 | 7.387 |
| 0.4978 | 876.3 | 0.473 | 0.471 | −0.009 | 1.4431 | 13.617 | 0.9309 | 903.7 | 0.380 | 0.379 | −0.002 | 1.3709 | 4.542 |
| 0.6000 | 881.8 | 0.450 | 0.448 | −0.008 | 1.4286 | 12.893 | | | | | | | |
| Ethyl Formate (1) + Ethylbenzene (2) at 313.15 K | | | | | | | | | | | | | |
| 0.1478 | 853.7 | 0.502 | 0.500 | −0.007 | 1.4791 | 5.836 | 0.6925 | 875.9 | 0.391 | 0.388 | −0.009 | 1.4142 | 11.165 |
| 0.2728 | 857.7 | 0.476 | 0.471 | −0.008 | 1.4682 | 9.481 | 0.7768 | 880.0 | 0.376 | 0.374 | −0.007 | 1.4042 | 10.409 |
| 0.3884 | 861.8 | 0.452 | 0.446 | −0.009 | 1.4532 | 11.789 | 0.8510 | 885.1 | 0.363 | 0.362 | −0.006 | 1.3921 | 8.006 |
| 0.4978 | 866.3 | 0.420 | 0.424 | −0.010 | 1.4415 | 13.017 | 0.9309 | 891.7 | 0.351 | 0.349 | −0.002 | 1.3695 | 3.937 |
| 0.6000 | 873.2 | 0.409 | 0.398 | −0.010 | 1.4269 | 12.923 | | | | | | | |
| Ethyl Benzoate + *o*-Xylene (2) at 303.15 K | | | | | | | | | | | | | |
| 0.0847 | 887.3 | 0.758 | 0.750 | −0.026 | 1.4994 | 6.352 | 0.5600 | 972.3 | 1.190 | 1.156 | −0.095 | 1.5009 | 18.946 |
| 0.1749 | 904.2 | 0.837 | 0.813 | −0.042 | 1.4996 | 11.048 | 0.6668 | 988.1 | 1.312 | 1.278 | −0.085 | 1.5010 | 16.886 |
| 0.2686 | 920.9 | 0.909 | 0.885 | −0.069 | 1.4999 | 15.869 | 0.7675 | 1001.3 | 1.433 | 1.403 | −0.070 | 1.5011 | 13.456 |
| 0.3579 | 937.5 | 1.000 | 0.960 | −0.072 | 1.5001 | 18.264 | 0.8768 | 1021.1 | 1.566 | 1.555 | −0.052 | 1.5013 | 7.912 |
| 0.4613 | 954.0 | 1.085 | 1.055 | −0.096 | 1.5007 | 19.514 | | | | | | | |
| Ethyl Benzoate (1) + *o*-Xylene(2) at 313.15 K | | | | | | | | | | | | | |
| 0.0847 | 879.3 | 0.676 | 0.666 | −0.014 | 1.4883 | 5.929 | 0.5600 | 963.8 | 1.015 | 0.990 | −0.063 | 1.4997 | 19.116 |
| 0.1749 | 896.1 | 0.732 | 0.717 | −0.032 | 1.4986 | 12.013 | 0.6668 | 980.8 | 1.113 | 1.083 | −0.053 | 1.4999 | 16.928 |
| 0.2686 | 913.1 | 0.800 | 0.776 | −0.040 | 1.4989 | 16.078 | 0.7675 | 992.7 | 1.208 | 1.179 | −0.040 | 1.5001 | 13.519 |
| 0.3579 | 930.2 | 0.864 | 0.835 | −0.049 | 1.4993 | 18.424 | 0.8768 | 1010.9 | 1.310 | 1.294 | −0.027 | 1.5003 | 7.688 |
| 0.4613 | 945.7 | 0.937 | 0.911 | −0.061 | 1.4995 | 19.776 | | | | | | | |
| Ethyl Benzoate (1) + *m*-Xylene (2) at 303.15 K | | | | | | | | | | | | | |
| 0.0887 | 871.6 | 0.612 | 0.611 | −0.051 | 1.4946 | 6.953 | 0.5707 | 966.5 | 1.055 | 1.040 | −0.182 | 1.4990 | 19.019 |
| 0.1713 | 887.2 | 0.676 | 0.672 | −0.085 | 1.4957 | 11.956 | 0.6576 | 981.7 | 1.161 | 1.167 | −0.179 | 1.4995 | 14.935 |
| 0.2626 | 905.2 | 0.759 | 0.735 | −0.111 | 1.4964 | 15.960 | 0.7831 | 1002.2 | 1.352 | 1.351 | −0.138 | 1.5003 | 12.095 |
| 0.3553 | 926.0 | 0.837 | 0.813 | −0.143 | 1.4970 | 18.427 | 0.8832 | 1018.5 | 1.500 | 1.511 | −0.109 | 1.5011 | 7.692 |
| 0.4588 | 946.8 | 0.931 | 0.915 | −0.172 | 1.4974 | 19.564 | | | | | | | |

**Table 2. (Continued)**

| $X_1$ | $\rho$/kg·m$^{-3}$ | $\eta$/mPa·s exptl | $\eta$/mPa·s eq 3 | $\Delta\eta$/mPa·s | $n_D$ | $\Delta R$/cm$^3$mol$^{-1}$ | $X_1$ | $\rho$/kg·m$^{-3}$ | $\eta$/mPa·s exptl | $\eta$/mPa·s eq 3 | $\Delta\eta$/mPa·s | $n_D$ | $\Delta R$/cm$^3$mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ethyl Benzoate (1) + *m*-Xylene (2) at 313.15 K | | | | | | | | | | | | | |
| 0.0887 | 857.3 | 0.547 | 0.552 | −0.043 | 1.4917 | 7.124 | 0.5707 | 966.5 | 0.910 | 0.896 | −0.129 | 1.4979 | 18.815 |
| 0.1713 | 875.0 | 0.601 | 0.598 | −0.066 | 1.4925 | 12.085 | 0.6576 | 971.7 | 0.997 | 0.982 | −0.123 | 1.4984 | 17.436 |
| 0.2626 | 895.5 | 0.664 | 0.654 | −0.088 | 1.4939 | 16.090 | 0.7831 | 993.7 | 1.146 | 1.126 | −0.090 | 1.4988 | 12.876 |
| 0.3553 | 917.5 | 0.732 | 0.740 | −0.106 | 1.4955 | 18.573 | 0.8832 | 1009.8 | 1.274 | 1.259 | −0.055 | 1.4993 | 7.697 |
| 0.4588 | 937.2 | 0.809 | 0.797 | −0.126 | 1.4963 | 19.748 | | | | | | | |
| Ethyl Benzoate (1) + *p*-Xylene (2) at 303.15 K | | | | | | | | | | | | | |
| 0.0916 | 871.1 | 0.622 | 0.623 | −0.052 | 1.4931 | 7.233 | 0.5703 | 964.8 | 1.045 | 1.053 | −0.195 | 1.4970 | 19.989 |
| 0.1757 | 889.3 | 0.679 | 0.681 | −0.095 | 1.4939 | 12.115 | 0.6730 | 982.8 | 1.181 | 1.185 | −0.180 | 1.4983 | 16.810 |
| 0.2719 | 908.4 | 0.765 | 0.756 | −0.122 | 1.4951 | 16.224 | 0.7781 | 1000.8 | 1.325 | 1.340 | −0.161 | 1.4988 | 13.659 |
| 0.3616 | 925.3 | 0.837 | 0.833 | −0.156 | 1.4957 | 18.607 | 0.8651 | 1022.8 | 1.469 | 1.486 | −0.120 | 1.4995 | 12.295 |
| 0.4681 | 947.1 | 0.951 | 0.938 | −0.168 | 1.4965 | 19.597 | 0.9370 | 1040.8 | 1.603 | 1.566 | −0.070 | 1.5001 | 3.928 |
| Ethyl Benzoate (1) + *p*-Xylene (2) at 313.15 K | | | | | | | | | | | | | |
| 0.0916 | 863.0 | 0.550 | 0.564 | −0.051 | 1.4912 | 6.919 | 0.5703 | 956.0 | 0.900 | 0.907 | −0.142 | 1.4963 | 19.139 |
| 0.1757 | 880.9 | 0.606 | 0.610 | −0.074 | 1.4924 | 11.996 | 0.6730 | 974.0 | 1.008 | 1.009 | −0.129 | 1.4972 | 16.928 |
| 0.2719 | 899.9 | 0.686 | 0.671 | −0.081 | 1.4948 | 16.296 | 0.7781 | 993.2 | 1.126 | 1.127 | −0.108 | 1.4979 | 13.040 |
| 0.3616 | 917.3 | 0.739 | 0.733 | −0.111 | 1.4950 | 18.646 | 0.8651 | 1010.2 | 1.239 | 1.240 | −0.075 | 1.4989 | 8.519 |
| 0.4681 | 937.5 | 0.825 | 0.825 | −0.123 | 1.4956 | 19.736 | 0.9370 | 1028.2 | 1.339 | 1.341 | −0.040 | 1.4996 | 4.247 |
| Ethyl Benzoate (1) + Ethylbenzene (2) at 303.15 K | | | | | | | | | | | | | |
| 0.0862 | 875.1 | 0.643 | 0.650 | −0.053 | 1.4920 | 6.570 | 0.5625 | 967.0 | 1.071 | 1.065 | −0.173 | 1.4968 | 18.938 |
| 0.1804 | 892.6 | 0.711 | 0.714 | −0.094 | 1.4932 | 12.202 | 0.6722 | 984.9 | 1.206 | 1.213 | −0.165 | 1.4971 | 16.643 |
| 0.2589 | 910.2 | 0.767 | 0.773 | −0.128 | 1.4934 | 15.558 | 0.7675 | 1002.0 | 1.330 | 1.337 | −0.150 | 1.4992 | 12.807 |
| 0.3522 | 927.2 | 0.857 | 0.851 | −0.145 | 1.4942 | 18.519 | 0.8678 | 1019.0 | 1.496 | 1.499 | −0.100 | 1.4998 | 8.324 |
| 0.4720 | 950.1 | 0.970 | 0.966 | −0.170 | 1.4960 | 19.493 | 0.9325 | 1040.9 | 1.615 | 1.615 | −0.055 | 1.5003 | 4.019 |
| Ethyl Benzoate (1) + Ethylbenzene (2) at 313.15 K | | | | | | | | | | | | | |
| 0.0862 | 867.0 | 0.570 | 0.582 | −0.046 | 1.4911 | 6.646 | 0.5625 | 960.4 | 0.937 | 0.917 | −0.107 | 1.4959 | 19.010 |
| 0.1804 | 884.3 | 0.629 | 0.635 | −0.071 | 1.4921 | 12.313 | 0.6722 | 976.2 | 1.063 | 1.023 | −0.080 | 1.4963 | 16.803 |
| 0.2589 | 901.3 | 0.682 | 0.683 | −0.089 | 1.4930 | 15.672 | 0.7675 | 993.0 | 1.169 | 1.127 | −0.060 | 1.4981 | 13.409 |
| 0.3522 | 918.1 | 0.745 | 0.746 | −0.110 | 1.4937 | 18.385 | 0.8678 | 1009.7 | 1.268 | 1.251 | −0.051 | 1.4992 | 8.505 |
| 0.4720 | 941.4 | 0.844 | 0.838 | −0.119 | 1.4954 | 19.672 | 0.9325 | 1027.4 | 1.335 | 1.339 | −0.035 | 1.4996 | 4.312 |

**Table 3. Parameters of Equation 2 and the Standard Deviations $\sigma(\Delta\eta)$ of Various Binary Systems**

| systems | $T$/K | $A_o$ | $A_1$ | $A_2$ | $\sigma(\Delta\eta)$/mPa·s |
|---|---|---|---|---|---|
| ethyl formate + *o*-xylene | 303.15 | −0.1075 | 0.0092 | -0.0387 | 0.002 |
| | 313.15 | −0.1210 | 0.0513 | 0.0191 | 0.004 |
| ethyl formate + *m*-xylene | 303.15 | −0.0664 | −0.0026 | 0.0262 | 0.003 |
| | 313.15 | −0.0506 | 0.0250 | 0.0172 | 0.002 |
| ethyl formate + *p*-xylene | 303.15 | −0.0476 | 0.0223 | −0.0182 | 0.003 |
| | 313.15 | −0.0790 | 0.0288 | 0.0381 | 0.005 |
| ethyl formate + ethyl benzene | 303.15 | −0.0317 | 0.0070 | −0.0001 | 0.001 |
| | 313.15 | −0.0410 | 0.0074 | −0.0070 | 0.001 |
| ethyl benzoate + *o*-xylene | 303.15 | −0.3480 | −0.0940 | −0.0559 | 0.007 |
| | 313.15 | −0.2374 | −0.0299 | 0.0362 | 0.003 |
| ethyl benzoate + *m*-xylene | 303.15 | −0.6797 | −0.2597 | −0.2238 | 0.008 |
| | 313.15 | −0.4987 | −0.0407 | −0.0370 | 0.005 |
| ethyl benzoate + *p*-xylene | 303.15 | −0.7117 | −0.2866 | −0.2500 | 0.006 |
| | 313.15 | −0.4996 | −0.0782 | −0.1769 | 0.009 |
| ethyl benzoate + ethyl benzene | 303.15 | −0.6906 | −0.1399 | −0.1277 | 0.004 |
| | 313.15 | −0.4096 | 0.0613 | −0.1755 | 0.010 |

stoppered bottles. The mixtures were completely miscible over the whole composition range. Densities were determined with a pycnometer having a bulb volume of about 20 cm$^3$ and a capillary internal diameter of about 1 mm. The pycnometer was calibrated at 303.15 K and 313.15 K with doubly distilled water. The corresponding uncertainty of the density determination is estimated to be better than ±0.2 kg·m$^{-3}$. The viscosities of the pure liquids and of the mixtures were determined using an Ubbelohde viscometer. The method and calibration of the viscometer has already been reported elsewhere.[17] Kinetic energy corrections were applied to viscosity data, and their uncertainties were estimated to be better than ±0.003 mPa·s. In making determinations, both the pycnometer and the viscometer were maintained in a thermostatic bath until at least three consecutive measurements of the liquid height in the capillaries or the flow time indicated that the sample had reached the temperature of the bath. The temperature of the water thermostat was controlled to ±0.01 K. A proportional integral control model was used to maintain the temperature in the thermostat to be within ±0.01 K of the desired value. The refractive indexes were measured using a thermostated Abbe refractometer (model R-8), which works with the wavelength corresponding to the D line of sodium. The prism was equipped with a tightly fitting lid that preserves the sample from preferential evaporation. The instrument calibration was carried out with doubly distilled water. An average of three measurements was taken for each sample mixture. The uncertainty of the refractive indexes thus estimated is found to be lower than $\pm 2 \times 10^{-4}$.

## Results and Discussion

Table 2 shows the experimental densities $\rho$, dynamic viscosities $\eta$, refractive indexes $n_D$, viscosity deviations $\Delta\eta$, and molar refraction deviations $\Delta R$ obtained for various binary mixtures at 303.15 K and 313.15 K. The dynamic viscosities of the mixtures were determined by multiplying the kinematic viscosity by the density of the mixture at the same composition. The viscosity deviations $\Delta\eta$ were obtained from dynamic viscosity composition data through

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{1}$$

where $\eta$, $\eta_1$, and $\eta_2$ are the dynamic viscosities of the mixture and pure components 1 (ester) and 2 (hydrocarbon), respectively. The $\Delta\eta$ values were correlated satisfactorily using the Redlich–Kister[21] equation

$$\Delta\eta = x_1x_2[A_o + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \tag{2}$$

where the values of fitting coefficients $A_o$, $A_1$, and $A_2$ were determined by a least-squares method. Table 3 shows the fitting coefficients and the standard deviations for each of the binary mixtures at the working temperature. It was observed that the average standard deviation value of the deviations of viscosity $\Delta\eta$ for all of the systems is 0.004 mPa·s at 303.15 K and 0.005 mPa·s at 313.15 K. The mixture viscosities have been recalculated from Frenkel,[22] the one-parameter empirical relation

$$\ln \eta = {x_1}^2 \ln \eta_1 + {x_2}^2 \ln \eta_2 + 2x_1x_2 \ln \eta_{12} \tag{3}$$

where the value of $\eta_{12}$ is obtained by the relation

$$\eta_{12} = 0.5\eta_1 + 0.5\eta_2$$

This value of $\eta_{12}$ was used to obtain $\eta$ at other compositions. The calculated viscosity results are included in Table 2. A perusal of Table 2 indicates that the agreement between the experimental and calculated values at both temperatures is good and within the experimental error. The deviations in molar refraction $\Delta R$ were calculated as a function of mole fraction $x_i$ using the following expression

$$\Delta R = R_M - \sum_i x_iR_i \tag{4}$$

where $R_M$ is molar refraction of the mixture obtained from the Lorentz–Lorentz equation[23] and $R_i$ is the molar refraction for component $i$. As noted from Table 2, the $\Delta\eta$ values were negative over the entire composition range for all of the systems in this study at both temperatures. The maximum of the $\Delta\eta$ values was located at about $x_1 = 0.5$. Furthermore, it was observed that in the case of systems containing ethyl formate the viscosity deviation was maximum for *o*-xylene and minimum for ethylbenzene whereas for systems of ethyl benzoates the deviation was maximum for *p*-xylene and minimum for *o*-xylene. These negative $\Delta\eta$ values were ascribed to the dominance of dispersion forces compared to the induced dipole–dipole interactions. The effect of temperature on the viscosity deviations can be justified because an increase in temperature caused an increase (less negative) in $\Delta\eta$ values except for mixtures of ethyl formate + *p*-xylene and ethyl formate + ethyl benzene, for which the $\Delta\eta$ values decrease (more negative) slightly. However, in comparison to the systems of ethyl formate the temperature effect was found to be more significant for the systems of ethyl benzoate. Figures 1 and 2 display the isothermal variations of the $\Delta\eta$ values with the mole fraction of ester. In general, the shapes of the curves were nearly symmetrical except those from the binary mixtures of ethyl formate + *p*-xylene that showed the maxima slightly skewed toward a lower ester mole fraction. The deviations in molar refraction $\Delta R$ values were positive over the entire composition range for all of the studied systems. The $\Delta R$ values were found to be similar at both temperatures, indicating that the effect of temperature on this property was negligible.

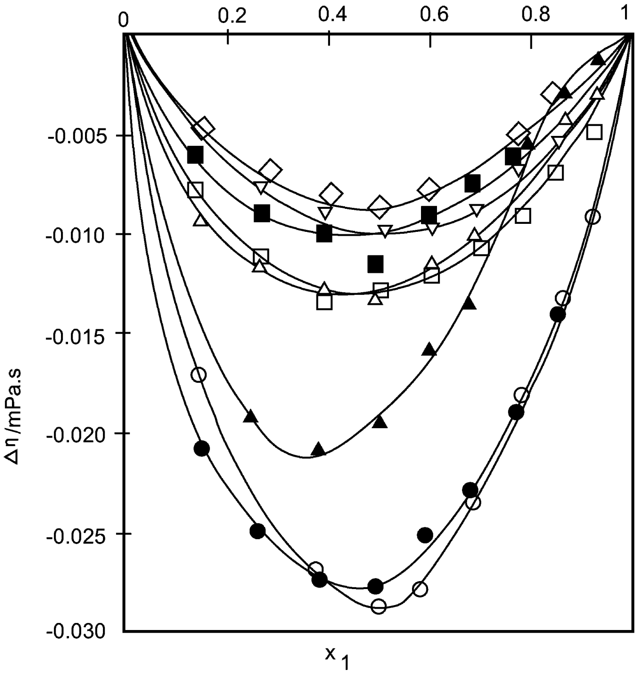

**Figure 1.** Deviations in viscosity $\Delta\eta$ vs mole fraction of ethyl formate + *o*-xylene (○), + *m*-xylene (□), + *p*-xylene (△), and + ethyl benzene (◇), respectively, at 303.15 K and for ethyl formate + *o*-xylene (●), + *m*-xylene (■), + *p*-xylene (▲), and + ethyl benzene (▽), respectively, at 313.15 K.

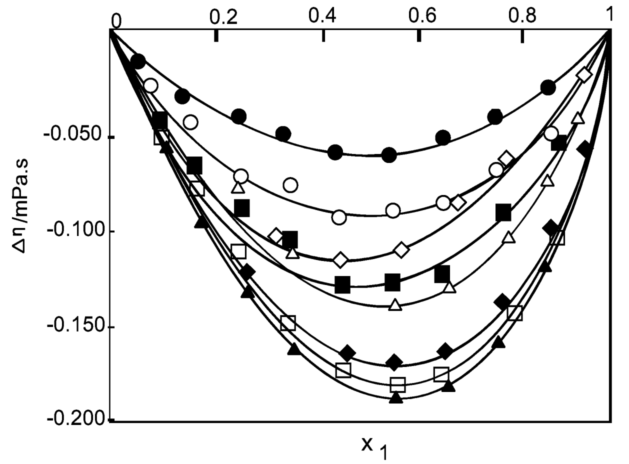

**Figure 2.** Deviations in viscosity $\Delta\eta$ vs mole fraction of ethyl benzoate + *o*-xylene (○), + *m*-xylene (□), + *p*-xylene (▲), and + ethyl benzene (◆), respectively, at 303.15 K and for ethyl benzoate + *o*-xylene (●), + *m*-xylene (■), + *p*-xylene (△), and + ethyl benzene (◇), respectively, at 313.15 K.

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