# CHAPTER XI

## Studies on Excess Molar Volumes and Viscosity Deviations of Binary Mixtures of Butylamine and N, N-dimethylformamide with Some Alkyl Acetates at 298.15 K*

### 11.1. Introduction

Studies on thermodynamic and transport properties are important in understanding the nature of molecular interactions in binary liquid mixtures. These properties are extremely useful for designing many types of transport and process equipment in chemical industries. There has been a recent upsurge of interest[1, 2] in the study of thermodynamic properties of binary liquid mixtures. These have been extensively used to obtain information on intermolecular interactions and stereo chemical effects in these systems. BA and DMF are versatile solvents used in the separation of saturated and unsaturated hydrocarbons and in pharmaceutical synthesis, and serve as solvents for many polymers.[3] In this chapter we report experimental data for density ($\rho$) and viscosity ($\eta$) of the following mixtures at 298.15 K: butylamine (BA) or N, N- dimethylformamide (DMF) + methyl acetate (MA), ethyl acetate (EA), butyl acetate (BUA), and iso-amyl acetate (AA). Using these data, excess molar volume ($V^E$), viscosity deviation ($\Delta\eta$), Grunberg- Nissan ($d_{12}$), Tamura- Kurata ($T_{12}$), and Hind ($H_{12}$) interaction parameters have been calculated. These results have been fitted to Redlich-Kister type polynomial equations to estimate the binary coefficients and standard errors between the experimental and calculated values.

### 11.2. Experimental Section

#### 11.2.1 *Materials*

Butylamine (S. D. Fine Chem, minimum assay GLC, 98%) was stored over sodium hydroxide pellets for several days and fractionally distilled twice.[4] N, N- dimethylformamide (S. D. Fine Chemicals, AR, purity>99%) was purified by the method described by Y. Zhao et al.[5] Methyl, ethyl, butyl and iso-amyl acetates (S. D. Fine Chemicals, AR, purity>99%) were used. Methyl acetate was washed with saturated solution of NaCl, dried with

*Published in Indian Journal of Chemistry, Sec-A

anhydrous $MgCl_2$, and then distilled. Ethyl acetate was dried over $K_2CO_3$, filtered, and distilled, and the first and the last portions of the distillate were discarded. The entire middle fraction was then distilled over $P_2O_5$. Butyl acetate and iso-amyl acetate were purified by drying over $CaCO_3$ overnight, filtered, and freshly distilled. The densities and viscosities of the solvents at 298.15 K were in good agreement with the literature values [5-8] as given in Table 1 and the purity of the solvents used in the present study is expected to be about 99.5%.

#### 11.2.2 *Apparatus and procedures*

Densities ($\rho$) at 298.15 K were measured with an Ostwald –Sprengel type pycnometer having a bulb volume of about 25 $cm^3$ and the capillary of internal diameter of about 1 mm. The measurements were done in a thermostated bath controlled to ± 0.1 K. The viscosity was measured by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from the literature. The flow times were accurate to ± 0.1s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was ± 2 x $10^{-4}$ mPa.s. The details of the methods and techniques have been described earlier.[9-11] The mixtures were prepared by mixing known volumes of pure liquids in airtight-stoppered bottles. The reproducibility in mole fraction was within ± 0.0002 units. The mass measurements accurate to ± 0.01mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The precision of density measurements was ± 3 x $10^{-4}$ g $cm^{-3}$.

## 11.3. Results and discussion

### 11.3.1. Excess Molar Volume

The experimental viscosities, densities, excess volumes ($V^E$), viscosity deviations ($\Delta\eta$) for the binary mixtures studied at 298.15 K are presented in Table 2. The excess molar volumes ($V^E$) were calculated using the equation,

$$V^E = \sum_{i=1}^{J} x_i M_i (1/\rho - 1/\rho_i) \qquad (1)$$

where $\rho$ is the density of the mixture and $M_i$, $x_i$ and $\rho_i$ are the molecular weight, mole fraction and density of $i^{th}$ component in the mixture,

respectively. The estimated uncertainty for excess molar volumes ($V^E$) is ± 0.005 $cm^3.mol^{-1}$. From Table 2, it is observed that excess molar volumes ($V^E$) for all the BA systems, except for that involving MA, are positive over the entire range of composition. The positive values of excess volumes ($V^E$) for the three systems follow the order:

BA + AA > BA + BUA > BA + EA

The excess molar volumes ($V^E$) for all the DMF systems are negative and their negative values follow the order:

DMF + MA > DMF + EA> DMF + BUA > DMF + AA

The negative values of excess molar volume ($V^E$) suggest specific interactions[12, 13] between the unlike molecules in the systems while its positive values suggest dominance of dispersion forces[12, 13] between them. Treszczanowicz et al.[14] suggested that $V^E$ is the result of contributions from several opposing effects. These may be divided arbitrary into three types, namely, physical, chemical, and structural. Physical contributions contribute a positive term to $V^E$. The chemical or specific intermolecular interactions result in a volume decrease and contribute negative values to $V^E$. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes in the free volume. The actual volume change, therefore, depends on the relative strength of these effects. The negative values of excess molar volume ($V^E$) for all the mixtures studied may be attributed to dipole-induced dipole interactions between the unlike molecules in the binary mixtures through hydrogen bonding. The plots of excess molar volume ($V^E$) versus mole fraction ($x_1$) of BA or DMF for the binary mixtures are presented in figures 1 and 2. It is evident from the values of $V^E$ that for both the binary systems, the degree of specific intermolecular interactions between unlike molecules in the binary mixtures decreases as the chain length of the alkyl acetate increases. The excess enthalpy values determined by Venkatesu et al.[15] for DMF + EA and DMF + BUA mixtures also report similar results.

### 11.3.2. Viscosity Deviation

The deviation in viscosities ($\Delta\eta$) can be computed using the relationship,

$$\Delta\eta = \eta - \sum_{i=1}^{j}(x_i\eta_i) \qquad (2)$$

where $\eta$ is the dynamic viscosities of the mixture and $x_i$, $\eta_i$ are the mole fraction and viscosity of $i^{th}$ component in the mixture, respectively. The estimated uncertainty for viscosity deviation ($\Delta\eta$) is ± 0.004 mPa.s. A perusal of Table 2 shows that the values of viscosity deviation ($\Delta\eta$) are negative over the entire composition range for all the binary mixtures studied and the negative values increase as the chain length of the alkyl acetates increases. It is observed in many systems that there is no simple correlation between the strength of the interactions and the observed properties. Rastogi et al.[16] therefore, suggested that the observed excess property is a combination of an interaction and a non-interaction part. The non-interaction part in the form of size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter. In general, the negative values imply the presence of dispersion forces[17] in these mixtures; while positive values may be attributed to the presence of specific interactions.[17] The plots of viscosity deviation ($\Delta\eta$) versus mole fraction ($x_1$) for the different binary mixtures of BA and DMF have been presented in figures 3 and 4, respectively. The $\Delta\eta$ values for all the binary mixtures studied supported the results obtained from the values of $V^E$ discussed earlier.

### 11.3.3. Correlation Equations

Several semiempirical models have been proposed to estimate the dynamic viscosity ($\eta$) of the binary liquid mixtures in terms of pure-component data.[18, 19] Some of these that we examined are as follows:
Grunberg and Nissan[20] have suggested the following logarithmic relation between the viscosity of the binary mixtures and the pure components:

$$\eta = \exp[\sum_{i=1}^{j}(x_i \ln\eta_i) + d_{12}\prod_{i=1}^{j}x_i] \qquad (3)$$

where $d_{12}$ is a constant proportional to the interchange energy. It may be regarded as an approximate measure of the strength of molecular interactions between the mixing components.

Tamura-Kurata[21] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta = \sum_{i=1}^{j} x_i \phi_i \eta_i + 2T_{12} \prod_{i=1}^{j} [x_i \phi_i]^{1/2} \quad (4)$$

where $T_{12}$ is the interaction parameter and $\phi_i$ is the volume fraction of $i^{th}$ pure component in the mixture.

Molecular interactions may also be interpreted by the following viscosity model of Hind et al:[22]

$$\eta = \sum_{i=1}^{j} x_i^2 \eta_i + 2H_{12} \prod_{i=1}^{j} x_i \quad (5)$$

where $H_{12}$ is Hind interaction parameter, which may be attributed to unlike pair interaction.[23] The values of Grunberg-Nissan interaction parameter ($d_{12}$), the values of interaction parameters $T_{12}$ and $H_{12}$ have been calculated as a function of the composition of the binary mixtures of BA and DMF with MA, EA, BUA and AA, and were presented in Table 3.

From Table 3, it is seen that the values of $d_{12}$ are negative for all the binary systems studied, except for the mixtures of DMF + MA. The negative values of $d_{12}$ indicate the presence of dispersion forces[17] or weak specific interaction while its positive values indicate the presence of strong specific interactions[17] between the unlike molecules in the binary mixtures. Also for a given binary mixture, it has been observed that the values of $T_{12}$ and $H_{12}$ do not differ appreciably from each other. This is in agreement with the view put forward by Fort and Moore[17] in regard to the nature of parameter $T_{12}$ and $H_{12}$.

The excess properties ($V^E$ and $\Delta\eta$) were fitted to the Redlich-Kister polynomial equation,

$$Y^E = x_1 x_2 \sum_{i=1}^{k} a_i (x_1 - x_2)^i \quad (6)$$

where $Y^E$ refers to excess properties and $x_1$ and $x_2$ are the mole fraction BA or DMF and other component, respectively. The coefficients, $a_i$, were obtained by fitting equation (6) to experimental results using a least-squares regression method. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation

($\sigma$). The calculated values of $a_i$ along with the tabulated standard deviations ($\sigma$) are listed in Table 4. The standard deviation ($\sigma$) was calculated using,

$$\sigma = [(Y^E_{exp} - Y^E_{cal})^2/(n-m)]^{1/2} \quad (7)$$

where $n$ is the number of data points and $m$ is the number of coefficients. From Table 4, it is observed that the fits were good as presented by the small values of standard deviation ($\sigma$).

In the eight binary mixtures studied, it is really interesting to note that $V^E$ and $\Delta\eta$ have maxima/minima in the mole fraction range $x_1$ = 0.5 to 0.7 (Table 2). This indicates that specific interaction between the component molecules is predominated by hydrogen bonding. The maximum/minimum points are clear indication of the highest point of interaction between the component molecules in the binary mixtures.

## 11.4. Conclusion

In summary, the $V^E$ and $\Delta\eta$ values for the eight binary mixtures studied indicate that the degree of specific interactions between the mixing components decreases as the chain length of the alkyl acetates increases. This is in line with the concept of +I-effect of the alkyl groups of the alkyl acetates.

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Table 1.
Comparison of experimental density and viscosity of pure liquids with literature values at 298.15 K.

| Pure liquids | $\rho \times 10^{-3}$ (kg.m$^{-3}$) | | $\eta$ (mPa.s) | |
|---|---|---|---|---|
| | Exp. | Lit. | Exp. | Lit. |
| Butylamine | 0.7319 | 0.7331 [6] | 0.4934 | 0.496 [7] |
| N, N- Dimethylformamide | 0.9442 | 0.9440 [5] | 0.8016 | 0.802 [5] |
| Methyl Acetate | 0.9261 | 0.9268 [8] | 0.3798 | 0.384 [8] |
| Ethyl Acetate | 0.8941 | 0.894 [8] | 0.4233 | 0.428 [8] |
| Butyl Acetate | 0.8744 | 0.8762 [8] | 0.6684 | 0.674 [8] |
| Iso- amyl Acetate | 0.8660 | 0.8662 [8] | 0.7822 | 0.781 [8] |

Table2.
Values of density ($\rho$), viscosity ($\eta$), excess molar volume ($V^E$), viscosity deviation ($\Delta\eta$) for the binary mixtures of BA or DMF (1) with some alkyl acetates (2) at 298.15 K.

| Mole fraction ($x_1$) | $\rho \times 10^{-3}$ (kg. m$^{-3}$) | $\eta$ (mPa.s) | $V^E \times 10^6$ (m$^3$. mol$^{-1}$) | $\Delta\eta$ (mPa.s) |
|---|---|---|---|---|
| | | BA (1) + MA (2) | | |
| 0 | 0.9261 | 0.3798 | 0 | 0 |
| 0.1011 | 0.9032 | 0.3847 | -0.090 | -0.007 |
| 0.2020 | 0.8827 | 0.3889 | -0.308 | -0.014 |
| 0.3027 | 0.8653 | 0.3942 | -0.740 | -0.020 |
| 0.4031 | 0.8501 | 0.4024 | -1.330 | -0.023 |
| 0.5032 | 0.8352 | 0.4109 | -1.894 | -0.026 |
| 0.6031 | 0.8191 | 0.4211 | -2.270 | -0.027 |
| 0.7027 | 0.7998 | 0.4359 | -2.200 | -0.024 |
| 0.8020 | 0.7776 | 0.4516 | -1.685 | -0.019 |
| 0.9011 | 0.7535 | 0.4701 | -0.770 | -0.012 |
| 1 | 0.7319 | 0.4934 | 0 | 0 |
| | | BA (1) + EA (2) | | |
| 0 | 0.8941 | 0.4233 | 0 | 0 |
| 0.1180 | 0.8741 | 0.4059 | 0.070 | -0.026 |
| 0.2315 | 0.8546 | 0.3973 | 0.181 | -0.042 |
| 0.3405 | 0.8364 | 0.3923 | 0.240 | -0.055 |
| 0.4454 | 0.8188 | 0.3929 | 0.300 | -0.062 |
| 0.5464 | 0.8015 | 0.3967 | 0.431 | -0.065 |
| 0.6437 | 0.7860 | 0.4071 | 0.403 | -0.061 |
| 0.7376 | 0.7720 | 0.4192 | 0.259 | -0.056 |
| 0.8281 | 0.7588 | 0.4353 | 0.091 | -0.046 |
| 0.9156 | 0.7454 | 0.4591 | 0.010 | -0.028 |
| 1 | 0.7319 | 0.4934 | 0 | 0 |
| | | BA (1) + BUA (2) | | |
| 0 | 0.8744 | 0.6684 | 0 | 0 |
| 0.1500 | 0.8570 | 0.6056 | 0.101 | -0.036 |
| 0.2842 | 0.8398 | 0.5618 | 0.269 | -0.057 |
| 0.4050 | 0.8235 | 0.5299 | 0.389 | -0.068 |
| 0.5143 | 0.8080 | 0.5081 | 0.469 | -0.070 |
| 0.6136 | 0.7931 | 0.4887 | 0.530 | -0.072 |
| 0.7043 | 0.7802 | 0.4786 | 0.391 | -0.066 |
| 0.7875 | 0.7680 | 0.4715 | 0.211 | -0.059 |
| 0.8640 | 0.7558 | 0.4714 | 0.100 | -0.046 |
| 0.9346 | 0.7439 | 0.4753 | 0.020 | -0.029 |
| 1 | 0.7319 | 0.4934 | 0 | 0 |
| | | BA (1) + AA (2) | | |
| 0 | 0.8660 | 0.7822 | 0 | 0 |
| 0.1651 | 0.8493 | 0.6901 | 0.181 | -0.044 |
| 0.3080 | 0.8329 | 0.6290 | 0.400 | -0.064 |
| 0.4327 | 0.8171 | 0.5855 | 0.590 | -0.072 |
| 0.5427 | 0.8024 | 0.5512 | 0.680 | -0.074 |

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|---|---|---|---|---|
| 0.6403 | 0.7885 | 0.5200 | 0.730 | -0.077 |
| 0.7275 | 0.7766 | 0.5003 | 0.539 | -0.072 |
| 0.8059 | 0.7650 | 0.4865 | 0.371 | -0.063 |
| 0.8768 | 0.7538 | 0.4778 | 0.210 | -0.051 |
| 0.9412 | 0.7428 | 0.4780 | 0.090 | -0.032 |
| 1 | 0.7319 | 0.4934 | 0 | 0 |
| | | DMF (1) + MA (2) | | |
| 0 | 0.9261 | 0.3798 | 0 | 0 |
| 0.1012 | 0.9292 | 0.4148 | -0.112 | -0.008 |
| 0.2022 | 0.9320 | 0.4504 | -0.193 | -0.015 |
| 0.3028 | 0.9347 | 0.4858 | -0.275 | -0.022 |
| 0.4032 | 0.9372 | 0.5236 | -0.331 | -0.026 |
| 0.5034 | 0.9393 | 0.5636 | -0.349 | -0.028 |
| 0.6032 | 0.9412 | 0.6045 | -0.357 | -0.030 |
| 0.7028 | 0.9425 | 0.6504 | -0.312 | -0.026 |
| 0.8021 | 0.9435 | 0.6976 | -0.242 | -0.020 |
| 0.9012 | 0.9438 | 0.7482 | -0.117 | -0.012 |
| 1 | 0.9442 | 0.8016 | 0 | 0 |
| | | DMF (1) + EA (2) | | |
| 0 | 0.8941 | 0.4233 | 0 | 0 |
| 0.1181 | 0.8998 | 0.4567 | -0.100 | -0.011 |
| 0.2316 | 0.9056 | 0.4896 | -0.198 | -0.021 |
| 0.3406 | 0.9113 | 0.5232 | -0.267 | -0.029 |
| 0.4456 | 0.9168 | 0.5591 | -0.315 | -0.033 |
| 0.5466 | 0.9220 | 0.5955 | -0.330 | -0.035 |
| 0.6439 | 0.9269 | 0.6339 | -0.308 | -0.033 |
| 0.7377 | 0.9316 | 0.6737 | -0.264 | -0.029 |
| 0.8282 | 0.9359 | 0.7153 | -0.183 | -0.021 |
| 0.9156 | 0.9400 | 0.7573 | -0.086 | -0.012 |
| 1 | 0.9442 | 0.8016 | 0 | 0 |
| | | DMF (1)+ BUA (2) | | |
| 0 | 0.8744 | 0.6684 | 0 | 0 |
| 0.1501 | 0.8816 | 0.6705 | -0.091 | -0.018 |
| 0.2843 | 0.8891 | 0.6761 | -0.206 | -0.030 |
| 0.4051 | 0.8963 | 0.6849 | -0.258 | -0.037 |
| 0.5144 | 0.9035 | 0.6955 | -0.282 | -0.041 |
| 0.6138 | 0.9107 | 0.7082 | -0.296 | -0.042 |
| 0.7045 | 0.9177 | 0.7247 | -0.272 | -0.037 |
| 0.7876 | 0.9243 | 0.7431 | -0.213 | -0.030 |
| 0.8641 | 0.9311 | 0.7612 | -0.156 | -0.022 |
| 0.9346 | 0.9375 | 0.7797 | -0.070 | -0.013 |
| 1 | 0.9442 | 0.8016 | 0 | 0 |
| | | DMF (1)+ BUA (2) | | |
| 0 | 0.8660 | 0.7822 | 0 | 0 |
| 0.1652 | 0.8738 | 0.7649 | -0.086 | -0.020 |
| 0.3081 | 0.8819 | 0.7531 | -0.192 | -0.035 |
| 0.4329 | 0.8898 | 0.7483 | -0.233 | -0.042 |
| 0.5429 | 0.8977 | 0.7469 | -0.247 | -0.046 |
| 0.6404 | 0.9054 | 0.7481 | -0.228 | -0.046 |

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|---|---|---|---|---|
| 0.7277 | 0.9133 | 0.7548 | -0.213 | -0.041 |
| 0.8061 | 0.9210 | 0.7648 | -0.172 | -0.033 |
| 0.8769 | 0.9287 | 0.7750 | -0.118 | -0.024 |
| 0.9413 | 0.9363 | 0.7869 | -0.046 | -0.014 |
| 1 | 0.9442 | 0.8016 | 0 | 0 |

Table 3.
Grunberg-Nissan interaction parameter ($d_{12}$), Tamura- Kurata parameter ($T_{12}$), and Hind parameter ($H_{12}$) for the binary mixtures of BA or DMF (1) with some alkyl acetates (2) at 298.15 K.

| $x_1$ | $d_{12}$ | $T_{12}$ | $H_{12}$ |
|---|---|---|---|
| | BA (1) + MA (2) | | |
| 0.1011 | -0.1503 | 0.3997 | 0.4003 |
| 0.2020 | -0.1803 | 0.3927 | 0.3938 |
| 0.3027 | -0.1992 | 0.3874 | 0.3892 |
| 0.4031 | -0.1983 | 0.3855 | 0.3884 |
| 0.5032 | -0.2113 | 0.3806 | 0.3846 |
| 0.6031 | -0.2274 | 0.3746 | 0.3799 |
| 0.7027 | -0.2204 | 0.3733 | 0.3799 |
| 0.8020 | -0.2311 | 0.3677 | 0.3758 |
| 0.9011 | -0.2511 | 0.3591 | 0.3692 |
| | BA (1) + EA (2) | | |
| 0.1180 | -0.5774 | 0.3354 | 0.3349 |
| 0.2315 | -0.5554 | 0.3399 | 0.3397 |
| 0.3405 | -0.5715 | 0.3361 | 0.3361 |
| 0.4454 | -0.5778 | 0.3335 | 0.3336 |
| 0.5464 | -0.5996 | 0.3271 | 0.3274 |
| 0.6437 | -0.6001 | 0.3242 | 0.3247 |
| 0.7376 | -0.6343 | 0.3135 | 0.3142 |
| 0.8281 | -0.6945 | 0.2957 | 0.2967 |
| 0.9156 | -0.7623 | 0.2740 | 0.2753 |
| | BA (1) + BUA (2) | | |
| 0.1500 | -0.4148 | 0.4158 | 0.4381 |
| 0.2842 | -0.4302 | 0.4244 | 0.4410 |
| 0.4050 | -0.4532 | 0.4288 | 0.4406 |
| 0.5143 | -0.4726 | 0.4327 | 0.4402 |
| 0.6136 | -0.5349 | 0.4252 | 0.4284 |
| 0.7043 | -0.5768 | 0.4223 | 0.4212 |
| 0.7875 | -0.6569 | 0.4104 | 0.4043 |
| 0.8640 | -0.7395 | 0.3977 | 0.3860 |
| 0.9346 | -0.9348 | 0.3605 | 0.3396 |
| | BA (1) + AA (2) | | |
| 0.1651 | -0.3566 | 0.4349 | 0.4768 |
| 0.3080 | -0.3572 | 0.4555 | 0.4869 |
| 0.4327 | -0.3674 | 0.4683 | 0.4918 |
| 0.5427 | -0.4026 | 0.4713 | 0.4882 |
| 0.6403 | -0.4918 | 0.4598 | 0.4700 |

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|---|---|---|---|
| 0.7275 | -0.5633 | 0.4535 | 0.4567 |
| 0.8059 | -0.6612 | 0.4414 | 0.4367 |
| 0.8768 | -0.8218 | 0.4165 | 0.4012 |
| 0.9412 | -1.0605 | 0.3763 | 0.3457 |
| | DMF (1) + MA (2) | | |
| 0.1012 | 0.1379 | 0.5514 | 0.5484 |
| 0.2022 | 0.1204 | 0.5482 | 0.5451 |
| 0.3028 | 0.0949 | 0.5425 | 0.5393 |
| 0.4032 | 0.0825 | 0.5394 | 0.5361 |
| 0.5034 | 0.0749 | 0.5372 | 0.5337 |
| 0.6032 | 0.0595 | 0.5324 | 0.5286 |
| 0.7028 | 0.0617 | 0.5327 | 0.5287 |
| 0.8021 | 0.0560 | 0.5303 | 0.5261 |
| 0.9012 | 0.0551 | 0.5294 | 0.5250 |
| | DMF (1) + EA (2) | | |
| 0.1181 | 0.0046 | 0.5802 | 0.5582 |
| 0.2316 | -0.0133 | 0.5756 | 0.5526 |
| 0.3406 | -0.0254 | 0.5723 | 0.5479 |
| 0.4456 | -0.0257 | 0.5721 | 0.5461 |
| 0.5466 | -0.0313 | 0.5703 | 0.5427 |
| 0.6439 | -0.0321 | 0.5698 | 0.5405 |
| 0.7377 | -0.0330 | 0.5694 | 0.5383 |
| 0.8282 | -0.0295 | 0.5704 | 0.5376 |
| 0.9156 | -0.0388 | 0.5671 | 0.5322 |
| | DMF (1) + BUA (2) | | |
| 0.1501 | -0.1893 | 0.6940 | 0.6648 |
| 0.2843 | -0.1978 | 0.6945 | 0.6608 |
| 0.4051 | -0.2045 | 0.6955 | 0.6572 |
| 0.5144 | -0.2150 | 0.6949 | 0.6521 |
| 0.6138 | -0.2268 | 0.6938 | 0.6464 |
| 0.7045 | -0.2262 | 0.6969 | 0.6449 |
| 0.7876 | -0.2222 | 0.7008 | 0.6447 |
| 0.8641 | -0.2300 | 0.7007 | 0.6401 |
| 0.9346 | -0.2591 | 0.6938 | 0.6270 |
| | DMF (1) + AA (2) | | |
| 0.1652 | -0.1914 | 0.7440 | 0.7176 |
| 0.3081 | -0.2134 | 0.7416 | 0.7096 |
| 0.4329 | -0.2237 | 0.7444 | 0.7058 |
| 0.5429 | -0.2395 | 0.7445 | 0.6996 |
| 0.6404 | -0.2616 | 0.7422 | 0.6909 |
| 0.7277 | -0.2697 | 0.7448 | 0.6872 |
| 0.8061 | -0.2699 | 0.7496 | 0.6864 |
| 0.8769 | -0.2846 | 0.7494 | 0.6798 |
| 0.9413 | -0.3097 | 0.7460 | 0.6689 |

Table 4.
Values of coefficients $a_i$ of equation (6) and their standard deviations ($\sigma$) for the excess properties ($V^E$ and $\Delta\eta$) of the binary mixtures of BA or DMF (1) + some alkyl acetates (2) at 298.15 K.

| Binary mixture | Excess property | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| BA + MA | $V^E$ x $10^6$ | -7.536 | -10.229 | 2.901 | 8.387 | 0.011 |
| | $\Delta\eta$ | -0.104 | -0.031 | - | - | 0.000 |
| BA + EA | $V^E$ x $10^6$ | 1.535 | 1.144 | -1.694 | -2.644 | 0.034 |
| | $\Delta\eta$ | -0.255 | -0.041 | -0.017 | -0.043 | 0.001 |
| BA + BUA | $V^E$ x $10^6$ | 1.940 | 1.047 | -2.131 | -1.934 | 0.030 |
| | $\Delta\eta$ | -0.283 | -0.035 | -0.109 | -0.084 | 0.001 |
| BA + AA | $V^E$ x $10^6$ | 2.685 | 1.678 | -1.981 | -2.086 | 0.029 |
| | $\Delta\eta$ | -0.297 | -0.044 | -0.184 | -0.095 | 0.002 |
| DMF + MA | $V^E$ x $10^6$ | -1.425 | -0.335 | 0.199 | 0.355 | 0.007 |
| | $\Delta\eta$ | -0.116 | -0.030 | -0.014 | - | 0.000 |
| DMF + EA | $V^E$ x $10^6$ | -1.301 | -0.275 | 0.163 | 0.203 | 0.002 |
| | $\Delta\eta$ | -0.136 | -0.027 | -0.263 | - | 0.000 |
| DMF + BUA | $V^E$ x $10^6$ | -1.162 | -0.376 | 0.264 | - | 0.009 |
| | $\Delta\eta$ | -0.164 | -0.037 | -0.069 | -0.081 | 0.001 |
| DMF + AA | $V^E$ x $10^6$ | -0.984 | -0.268 | 0.245 | - | 0.009 |
| | $\Delta\eta$ | -0.182 | -0.054 | - | - | 0.001 |

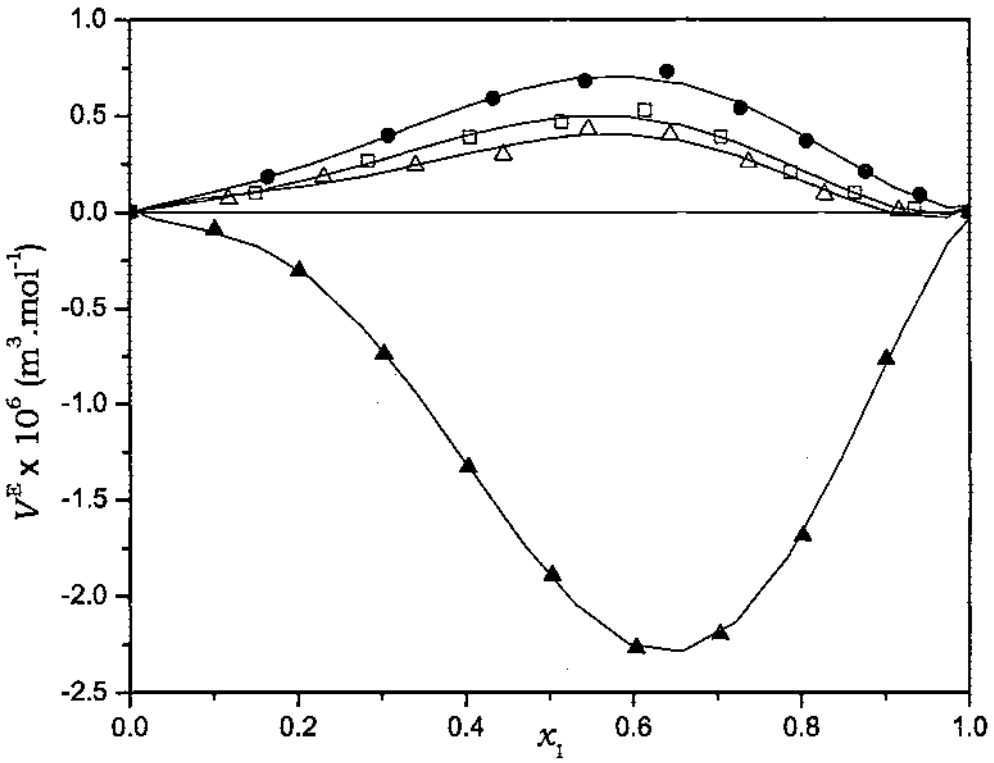


Figure 1.

Plots of excess molar volume ($V^E$) versus mole fraction of BA ($x_1$) at 298.15K for binary mixtures of BA with MA (▲), EA (Δ), BUA (□), AA (●).

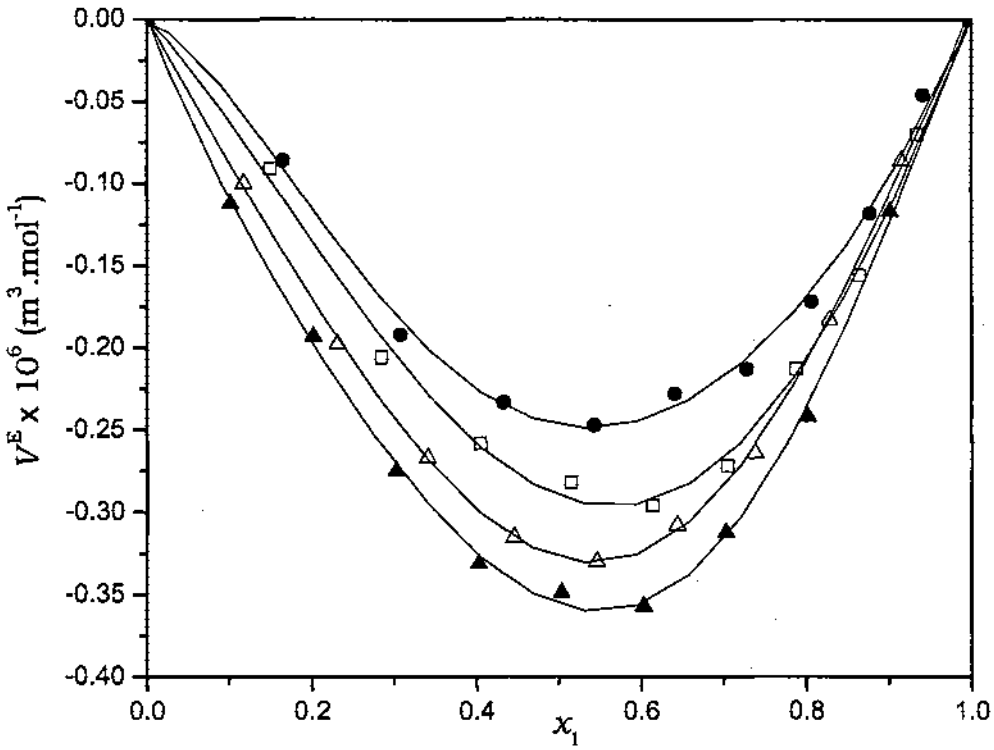


Figure 2.

Plots of excess molar volume ($V^E$) versus mole fraction of DMF ($x_1$) at 298.15K for binary mixtures of DMF with MA (▲), EA (Δ), BUA (□), AA (●).

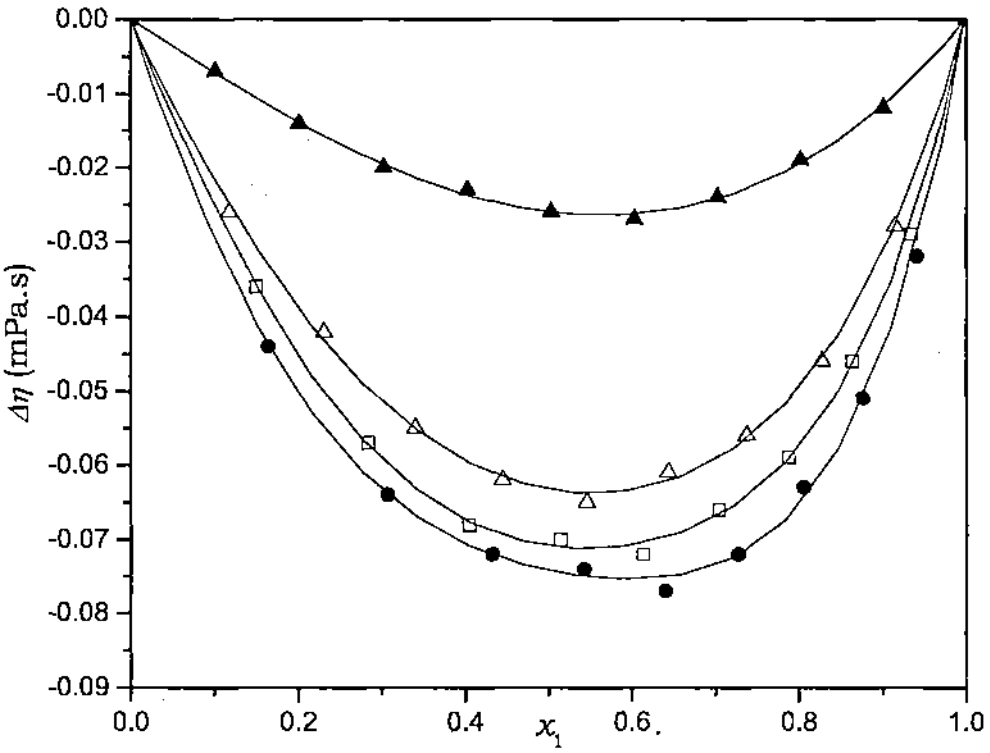


Figure 3.

Plots of viscosity deviation ($\Delta\eta$) versus mole fraction of BA ($x_1$) at 298.15 K for binary mixtures of BA with MA (▲), EA (Δ), BUA (□), AA (●).

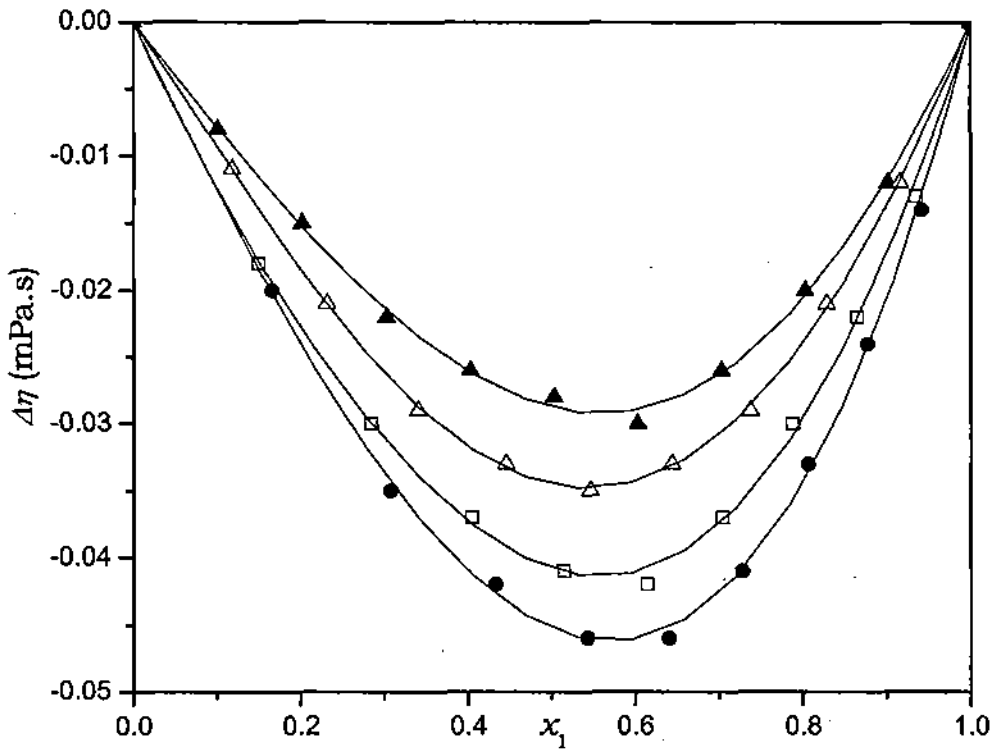


Figure 4. Plots of viscosity deviation ($\Delta\eta$) versus mole fraction of DMF ($x_1$) at 298.15K for binary mixtures of DMF with 1, MA (▲), 2, EA (Δ), 3, BUA (□), 4, AA (●).