# Densities, Viscosities, and Excess *Gibbs* Energy of Activation for Viscous Flow, for Binary Mixtures of Dimethyl Phthalate (*DMP*) with 1-Pentanol, 1-Butanol, and 1-Propanol at Two Temperatures

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**Summary.** Density ($\rho$) and viscosity ($\eta$) values of the binary mixtures of $DMP$ + 1-pentanol, 1-butanol, and 1-propanol over the entire range of mole fraction at 298.15 and 303.15 K were measured in atmospheric pressure. The excess molar volume ($V^E$), viscosity deviations ($\Delta\eta$), and excess *Gibbs* energy of activation for viscous flow ($G^{*E}$) were calculated from the experimental measurements. These results were fitted to *Redlich–Kister* polynomial equation to estimate the binary interaction parameters.

The viscosity data were correlated with equations of *McAllister*. The calculated functions have been used to explain the intermolecular interaction between the mixing components.

**Keywords.** Viscosity; Density; Intermolecular interaction; Alkanol; Dimethyl phthalate.

## Introduction

Density ($\rho$) and viscosity ($\eta$) of liquid mixtures are required in most engineering calculations where fluid flow or mixing is an important factor. Moreover, knowledge of the dependence of densities and viscosities of liquid mixtures on composition is of great interest from a theoretical stand point since it may lead to better cognition of the fundamental behavior of liquid systems. The studies of excess thermodynamic properties are of considerable interest in understanding the intermolecular interactions in binary liquid mixtures [1]. The knowledge of these properties is very important in many practical problems concerning mass transport and fluid flow. Alkanols are self − associated through hydrogen bonds and this association decreases with increase in molar mass of alkanols [1]. In the present study, density and absolute viscosity were measured for the binary mixtures of $DMP$ + 1-pentanol, 1-butanol, and 1-propanol at atmospheric pressure in 298.15 and 303.15 K.

The viscosity ($\eta$) data were correlated with equation of *McAllister* [2]. The variations of the excess properties with the molecular size of 1-alkanols and temperature were investigated. Although the physical property data of the pure components are available in the literature [3–7] no experimental data are available for these mixtures at the comparable conditions of this study. The chemical formula for $DMP$ is $C_{10}H_{10}O_4$ and the structure is:
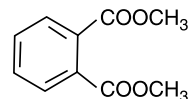


## Results and Discussion

Table 1 reports a comparison between the pure component density and viscosity at 298.15 K with the corresponding literature values. The measured results are in good agreement with literature values. The measured densities ($\rho_m$), viscosities ($\eta_m$), excess molar volume ($V^E$), and excess *Gibbs* energy of activation for viscous flow ($G^{*E}$) for the binary systems of $DMP$ + 1-pentanol, 1-butanol, and 1-propanol at

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**Table 1.** Pure component properties and their comparison with the literature values at 298.15 K

| Compound | Experimental $\rho/\mathrm{g \cdot cm^{-3}}$ | Ref. $\rho/\mathrm{g \cdot cm^{-3}}$ | Experimental $\eta/\mathrm{mPa \cdot s}$ | Ref. $\eta/\mathrm{mPa \cdot s}$ |
|---|---|---|---|---|
| *DMP* | 1.18657 | | 13.76169 | |
| 1-Pentanol | 0.81091 | 0.81090[a] | 3.48143 | 3.497[b] |
| 1-Butanol | 0.80645 | 0.8059[c] | 2.60264 | 2.5780[c] |
| 1-Propanol | 0.80017 | 0.79965[d] | 1.92971 | 1.9380[e] |

[a] Ref. [3]; [b] Ref. [4]; [c] Ref. [5]; [d] Ref. [6]; [e] Ref. [7]

**Table 2.** Densities, viscosities, excess molar volumes and *Gibbs* energy of activation for 1-pentanol (1) + DMP (2)

| $x_1$ | $\rho_m/$ g·cm$^{-3}$ | $\eta_m/$ mPa·s | $V_m^{\mathrm{E}}/$ cm$^3$·mol$^{-1}$ | $G^{*\mathrm{E}}/$ kJ·mol$^{-1}$ |
|---|---|---|---|---|
| | | 298.15 K | | |
| 0.00000 | 1.18657 | 13.76169 | 0.00000 | 0.00000 |
| 0.07318 | 1.16825 | 10.49876 | −0.05577 | −0.40976 |
| 0.14443 | 1.14938 | 8.68062 | −0.09248 | −0.62827 |
| 0.27525 | 1.11037 | 6.45156 | −0.20856 | −0.89997 |
| 0.39311 | 1.07599 | 5.24674 | −0.31571 | −1.00853 |
| 0.50273 | 1.03317 | 4.39616 | −0.33288 | −1.05816 |
| 0.60143 | 1.00063 | 3.88408 | −0.268557 | −1.04078 |
| 0.69355 | 0.96237 | 3.52054 | −0.17541 | −0.97346 |
| 0.77946 | 0.92410 | 3.29787 | −0.121608 | −0.84968 |
| 0.819208 | 0.90537 | 3.22913 | −0.096847 | −0.77091 |
| 0.93091 | 0.84915 | 3.17947 | −0.060811 | −0.44656 |
| 1.00000 | 0.81091 | 3.48143 | 0.00000 | 0.00000 |
| | | 303.15 K | | |
| 0.00000 | 0.18218 | 11.11102 | 0.00000 | 0.00000 |
| 0.07318 | 1.16381 | 8.51294 | −0.04208 | −0.41145 |
| 0.14443 | 1.14505 | 7.12532 | −0.08946 | −0.61192 |
| 0.27525 | 1.10814 | 5.20846 | −0.19549 | −0.95154 |
| 0.39311 | 1.07174 | 4.27968 | −0.30514 | −1.04993 |
| 0.50273 | 1.03407 | 3.79760 | −0.32231 | −0.98811 |
| 0.60143 | 0.99655 | 3.35259 | −0.25812 | −0.97734 |
| 0.69355 | 0.95839 | 3.00052 | −0.16482 | −0.95708 |
| 0.77946 | 0.92023 | 2.80635 | −0.110903 | −0.85175 |
| 0.819208 | 0.90155 | 2.74730 | −0.085275 | −0.78022 |
| 0.93091 | 0.84550 | 2.74817 | 0.051232 | −0.43566 |
| 1.00000 | 0.80745 | 3.01036 | 0.00000 | 0.00000 |

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

$$G^{*\mathrm{E}} = RT\left[\ln(V_m\eta_m) - \sum_{i-1}^{n} x_i \ln(V_i\eta_i)\right] \qquad (3)$$

where for each equation, $x$, $M$, $\rho$, $\eta$, and $V$ are the mole fraction, the molar mass, the density, the dynamic viscosity, and the molar volume, respectively.

**Table 3.** Densities, viscosities, excess molar volumes and *Gibbs* energy of activation for 1-butanol (1) + DMP (2)

| $x_1$ | $\rho_m/$ g·cm$^{-3}$ | $\eta_m/$ mPa·s | $V_m^{\mathrm{E}}/$ cm$^3$·mol$^{-1}$ | $G^{*\mathrm{E}}/$ kJ·mol$^{-1}$ |
|---|---|---|---|---|
| | | 298.15 K | | |
| 0.00000 | 1.18657 | 13.76169 | 0.00000 | 0.00000 |
| 0.08653 | 1.16815 | 10.47970 | −0.10374 | −0.29183 |
| 0.16799 | 1.14923 | 8.38940 | −0.17843 | −0.48551 |
| 0.311008 | 1.11207 | 5.90188 | −0.29721 | −0.73832 |
| 0.43671 | 1.07434 | 4.55780 | −0.37257 | −0.84544 |
| 0.54561 | 1.03650 | 3.83003 | −0.35683 | −0.82235 |
| 0.64397 | 0.99746 | 3.28653 | −0.28122 | −0.79844 |
| 0.72872 | 0.96000 | 2.95707 | −0.22856 | −0.72018 |
| 0.80659 | 0.92181 | 2.64327 | −0.18093 | −0.69217 |
| 0.84395 | 0.90221 | 2.55236 | −0.17895 | −0.63497 |
| 0.94088 | 0.84601 | 2.46473 | −0.14653 | −0.35545 |
| 1.00000 | 0.80645 | 2.60264 | 0.00000 | 0.00000 |
| | | 303.15 K | | |
| 0.00000 | 1.18218 | 11.11102 | 0.00000 | 0.00000 |
| 0.08653 | 1.16368 | 8.53398 | −0.09155 | −0.28538 |
| 0.16799 | 1.14477 | 6.79904 | −0.16607 | −0.50509 |
| 0.311008 | 1.10763 | 4.97815 | −0.28374 | −0.68349 |
| 0.43671 | 1.06991 | 3.91439 | −0.35557 | −0.76755 |
| 0.54561 | 1.03213 | 3.27852 | −0.34096 | −0.77142 |
| 0.64397 | 0.99322 | 2.81219 | −0.27271 | −0.76557 |
| 0.72872 | 0.95580 | 2.51506 | −0.21709 | −0.71675 |
| 0.80659 | 0.91771 | 2.29722 | −0.17207 | −0.64866 |
| 0.84395 | 0.89816 | 2.21965 | −0.17107 | −0.59628 |
| 0.94088 | 0.84207 | 2.16940 | −0.13618 | −0.30343 |
| 1.00000 | 0.80271 | 2.25262 | 0.00000 | 0.00000 |

298.15 and 303.15 K at atmospheric pressure are given in Tables 2–4 respectively.

The excess molar volume ($V^{\mathrm{E}}$), viscosity deviation ($\Delta\eta$), and excess *Gibbs* energy of activation for viscous flow ($G^{*\mathrm{E}}$) were calculated through the equations:

$$V^{\mathrm{E}} = \sum_{i-1}^{n} x_i M_i \left(\frac{1}{\rho_m} - \frac{1}{\rho_i}\right) \qquad (1)$$

**Table 4.** Densities, viscosities, excess molar volumes and *Gibbs* energy of activation for 1-propanol (1) + DMP (2)

| $x_1$ | $\rho_m/$ g·cm$^{-3}$ | $\eta_m/$ mPa·s | $V_m^E/$ cm$^3$·mol$^{-1}$ | $G^{*E}/$ kJ·mol$^{-1}$ |
|---|---|---|---|---|
| | | 298.15 K | | |
| 0.00000 | 1.18657 | 13.76169 | 0.00000 | 0.00000 |
| 0.10472 | 1.16791 | 9.89873 | −0.13388 | −0.25123 |
| 0.19594 | 1.14945 | 7.75954 | −0.21933 | −0.36919 |
| 0.35544 | 1.11204 | 5.41973 | −0.41202 | −0.42971 |
| 0.48519 | 1.07436 | 4.14735 | −0.49441 | −0.43842 |
| 0.59459 | 1.03538 | 3.35556 | −0.44991 | −0.42689 |
| 0.68696 | 0.99705 | 2.81788 | −0.44337 | −0.42200 |
| 0.76719 | 0.95735 | 2.47302 | −0.33161 | −0.37540 |
| 0.83632 | 0.91873 | 2.21454 | −0.29121 | −0.34228 |
| 0.86828 | 0.89897 | 2.12532 | −0.26600 | −0.30600 |
| 0.95178 | 0.84036 | 1.97112 | −0.16535 | −0.14330 |
| 1.00000 | 0.80017 | 1.92971 | 0.00000 | 0.00000 |
| | | 303.15 K | | |
| 0.00000 | 1.18218 | 11.11102 | 0.00000 | 0.00000 |
| 0.10472 | 1.16341 | 8.06634 | −0.11719 | −0.25519 |
| 0.19594 | 1.14495 | 6.41204 | −0.20090 | −0.36209 |
| 0.35544 | 1.10750 | 4.61243 | −0.38524 | −0.39067 |
| 0.48519 | 1.06984 | 3.58488 | −0.46552 | −0.39429 |
| 0.59459 | 1.03088 | 2.90604 | −0.41723 | −0.40613 |
| 0.68696 | 0.99229 | 2.47263 | −0.37767 | −0.39168 |
| 0.76719 | 0.95311 | 2.16898 | −0.31134 | −0.36798 |
| 0.83632 | 0.91442 | 1.95066 | −0.25602 | −0.34153 |
| 0.86828 | 0.89471 | 1.88699 | −0.23140 | −0.29376 |
| 0.95178 | 0.83628 | 1.73597 | −0.13401 | −0.17257 |
| 1.00000 | 0.79654 | 1.72896 | 0.00000 | 0.00000 |

The subscript *i* and *m* represent the pure components and the mixture, respectively. *R* is the gas constant and *T* is the absolute temperature. The composition dependence of the excess molar volume ($V^E$), viscosity deviation ($\Delta\eta$), and excess *Gibbs* energy of activation for viscous flow ($G^{*E}$) were represented by a *Redlich–Kister* [8] type of equation:

$$y = x_1 x_2 \sum_{i=0}^{p} a_i (x_1 - x_2)^i \qquad (4)$$

where *y* is $V^E, \Delta\eta$, or $G^{*E}$, $x_1$ and $x_2$ refer to the mole fractions of *DMP* and 1-alkanols, respectively.

In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation, $\delta$, as given by:

$$\delta = \left[ \sum (y_{exp} - y_{cal})^2 / (n - p) \right]^{\frac{1}{2}} \qquad (5)$$

where *n* is the total number of data points and *p* is the number of coefficients considered (Table 5). The experimental viscosity data of the binary mixtures were further fitted to the *McAllister* equation [2]:

$$\ln v_m = x_1^3 \ln v_1 + 3x_1^2 x_2 \ln A_{12} + 3x_1 x_2^2 \ln A_{21} + x_2^3 \ln v_2$$
$$- \ln\left[ x_1 + x_2 \frac{M_2}{M_1} \right] + 3x_1^2 x_2 \ln\left[ \frac{2 + (M_2/M_1)}{3} \right]$$
$$+ 3x_1 x_2^2 \ln\left[ \frac{1 + (2M_2/M_1)}{3} \right] + x_2^3 \ln\left[ \frac{M_2}{M_1} \right]$$
$$\qquad (6)$$

In this equation $v_m$ refers to the kinematic viscosity of the mixture of components 1 and 2, having mole fractions $x_1$ and $x_2$, respectively, $v_1$ and $v_2$ refer to the kinematic viscosity of pure liquids 1 and 2, respectively, and $A_{12}$ and $A_{21}$ represent the interaction parameters obtained by nonlinear regression analysis (Table 6).

Figure 1 shows that the excess molar volumes are negative for mixtures of *DMP* with all the alkanols studied here.

The $V^E$ values at equimolar concentrations of mixtures increase with increase of length of chain of 1-alkanols. The observed excess molar volume values in the present investigation may be discussed in terms of several effects which may be arbitrarily divided into physical, chemical and geometrical contributions. The physical interactions involve mainly dispersion forces giving a positive contribution to $V^E$.

The chemical or specific interactions between constituent molecules of the mixtures result in a volume decrease. The structural contributions arising from the geometrical fitting of one component into the other, due to differences in the molar volumes and free volumes between components lead to negative contributions to $V^E$. Figure 2 shows that the viscosity deviations, for all investigated systems, are negative throughout the mixture compositions. Negative viscosity deviations from rectilinear dependence on mole fraction may also occur, where dispersion forces are dominant, particularly for the system having different molecular size [9–11].
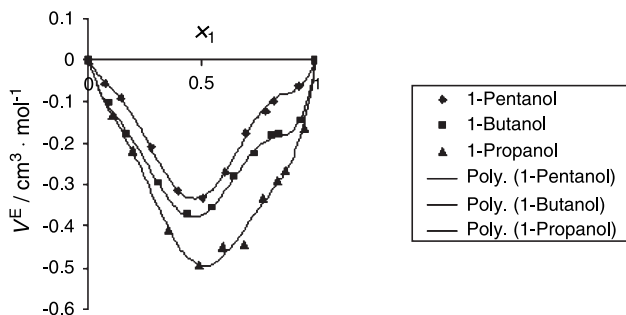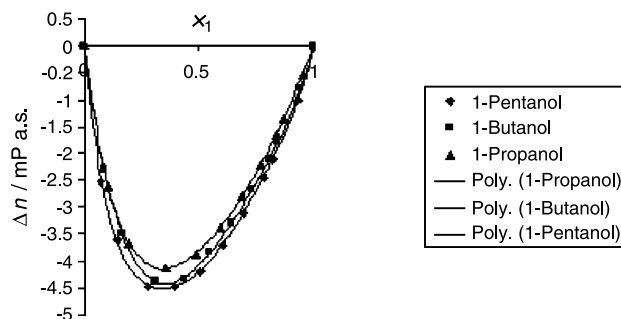
Figure 3 shows that the excess *Gibbs* energy of activation for viscous flow ($G^{*E}$) values, for all investigated system, are negative. *Meyer et al.* [12] state that excess *Gibbs* energy of activation for viscous flow, like viscosity deviations can be used to detect molecular interactions. The negative deviation values of $G^{*E}$ suggest the dominance of dispersion interaction between *DMP* and 1-alkanols molecules.

**Table 5.** Coefficients of *Redlich–Kister* equation and standard deviations

| | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $\delta$ |
|---|---|---|---|---|---|---|
| | | | 1-Pentanol + *DMP* | | | |
| | | | 298.15 K | | | |
| $V^E$ | −1.3245 | 0.4899 | 2.5498 | −0.8635 | −2.6934 | 0.00619 |
| $G^{*E}$ | −4.2446 | −0.1451 | −0.9606 | −0.3766 | −2.6148 | 0.01152 |
| $\Delta\eta$ | −16.8315 | 7.5536 | −5.4847 | 6.0566 | −9.7368 | 0.04310 |
| | | | 303.15 K | | | |
| $V^E$ | −1.2781 | 0.4874 | 2.5189 | −0.8321 | −2.4723 | 0.00708 |
| $G^{*E}$ | −4.0724 | 0.4990 | −2.8606 | −1.6154 | 0.0639 | 0.03179 |
| $\Delta\eta$ | −13.0563 | 5.4736 | −5.7183 | 5.0792 | −6.7033 | 0.04874 |
| | | | 1-Butanol + *DMP* | | | |
| | | | 298.15 K | | | |
| $V^E$ | −1.4905 | 0.5259 | 2.0405 | −1.3331 | −3.4570 | 0.00818 |
| $G^{*E}$ | −3.3691 | 0.1931 | −0.7068 | −2.3850 | −2.0581 | 0.01436 |
| $\Delta\eta$ | −16.3507 | 8.6272 | −5.2611 | 0.3755 | −3.6726 | 0.02655 |
| | | | 303.15 K | | | |
| $V^E$ | −1.4257 | 0.4950 | 1.9128 | −1.3054 | −3.1053 | 0.00747 |
| $G^{*E}$ | −3.0873 | −0.1678 | −1.8911 | −1.0627 | −0.1506 | 0.01017 |
| $\Delta\eta$ | −12.6094 | 6.1179 | −5.8065 | 1.9885 | −0.8760 | 0.02134 |
| | | | 1-Propanol + *DMP* | | | |
| | | | 298.15 K | | | |
| $V^E$ | −1.9757 | −0.1638 | 1.8071 | −0.8872 | −2.9173 | 0.02068 |
| $G^{*E}$ | −1.7431 | 0.1014 | −1.4712 | −0.2703 | −0.2409 | 0.02166 |
| $\Delta\eta$ | −15.2567 | 7.6107 | −5.9937 | 4.2169 | −2.3028 | 0.00771 |
| | | | 303.15 K | | | |
| $V^E$ | −1.8355 | −0.0375 | 1.7034 | −0.9682 | −2.4488 | 0.00941 |
| $G^{*E}$ | −1.5937 | 0.0270 | −1.4042 | −0.0962 | −0.9095 | 0.01136 |
| $\Delta\eta$ | −11.7453 | 5.4687 | −4.7164 | 4.0214 | −2.7281 | 0.00937 |

**Table 6.** Interactions parameters of *McAllister* equation and standard deviation

| Compound | Temperature/K | $A_{12}$ | $A_{21}$ | $\delta$ |
|---|---|---|---|---|
| 1-Pentanol | 298.15 | 2.8997 | 4.4242 | 0.1958 |
| + *DMP* | 303.15 | 2.4955 | 3.6404 | 0.1778 |
| 1-Butanol | 298.15 | 2.48681 | 4.70629 | 0.1169 |
| + *DMP* | 303.15 | 2.18671 | 3.96894 | 0.11371 |
| 1-Propanol | 298.15 | 2.59919 | 4.68797 | 0.11075 |
| + *DMP* | 303.15 | 2.27754 | 4.02007 | 0.11285 |



**Fig. 2.** Dependence of viscosity deviations, $\Delta\eta$, as function of mole fractions of alkanols for binary mixtures of 1-alkanols + *DMP* at 298.15 K

The chain lengths of 1-alkanols, molecular sizes, and shape have significant effect on the thermodynamic properties of the investigated systems.

## Experimental

*Materials*
*DMP*, 1-pentanol, 1-butanol, and 1-propanol were purchased from Fluka. The purities of these substances are more than



**Fig. 1.** Dependence of excess molar volumes, $V^E$, as function of mole fractions of alkanols for binary mixtures of 1-alkanols + *DMP* at 298.15 K
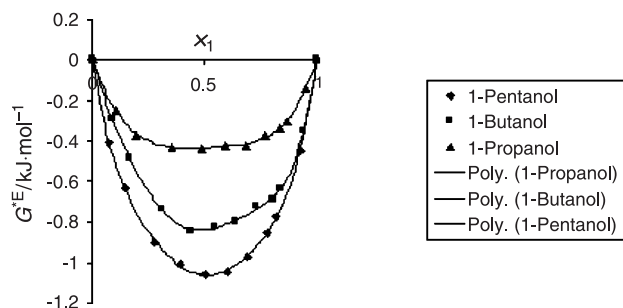
**Fig. 3.** Dependence of excess *Gibbs* energy of activation for viscous flow, $G^{*E}$, as function of mole fractions of alkanols for binary mixtures of 1-alkanols + *DMP* at 298.15 K

99 mol%. All reagents were used without further purification. Binary mixtures were prepared by known masses of each liquid in air-tight stoppered glass bottles.

*Instruments*

The mass measurements were made on a single pan Mettler balance to an accuracy of $\pm 0.0001$ g. No buoyancy corrections were applied. The possible error in mole fraction is calculated to be less than $\pm 1 \times 10^{-4}$.

Density $(\rho)$ measurements of pure components and binary mixtures over the complete composition range were carried out using *Anton Paar* oscillating u-tube densitometer (DMA 58), with $\pm 10^{-5}$ g cm$^{-3}$ accuracy at 298.15 and 303.15 K.

It was calibrated with double – distilled water and air [6, 13]. The temperatures were regulated using a circulating bath Heto DBT with a precision of $\pm 0.01$ K.

The kinematic viscosity was measured with *Ubbelohde* viscometers with a Schott-Geräte automatic measuring unit model AVS 400 provided with a transparent thermostat, which allows temperature stabilization with a tolerance of 0.01 K. Capillary diameters of 0.63 and 0.84 mm were used for kinematic viscosity ranges of 1.2–10 and 3–30 cSt. Each time 15 cm$^3$ of solution were measured. The calibration was carried out with double distilled water and glycerol (60% *w/v*). The uncertainty of the viscosity measurement was $< \pm 0.7\%$.

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