# Studies of viscosity and excess molar volume of binary mixtures 4. 1-Alkanol + tri-*n*-butylamine mixtures at 303.15 and 313.15 K

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## Abstract

The excess molar volume $V^E$, the viscosity deviation $\Delta \eta$ and the excess Gibbs energy of activation $\Delta G^{*E}$ of viscous flow are calculated from density and viscosity measurements of six mixtures of 1-propanol, 1-butanol, 1-pentanol, 1-heptanol, 1-octanol and 1-decanol with tri-*n*-butylamine over the entire range of mole fractions at 303.15 and 313.15 K. The values of $V^E$ of all six systems are very large and negative. Except for 1-propanol + tri-*n*-butylamine, the magnitude of negative deviations in viscosity increases with chain length of alkanol. The results have been explained considering mixed associated species of type $A_iB$ involving alkanol (A) with tri-*n*-butylamine (B) through O–H$\cdots$N bonds. The viscosity data have been correlated with the equations of Grunberg and Nissan, Tamura and Kurata, Hind, McLaughlin and Ubbelohde, Katti and Chaudhri, McAllister, Heric, and of Auslaender.
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## 1. Introduction

In previous papers [1–3], we have reported the viscosities $\eta$ and the excess molar volumes $V^E$ of binary mixtures of primary and secondary alkylamines with a series of 1-alkanols at 303.15 and 313.15 K. The 1-alkanol (A) and the primary or secondary amine (B) have both, a proton donor and a proton acceptor group. Besides AB, and $A_iB$ mixed associates the species of type $A_iB_j$ also exists [4]. The latter species that contain many monomers can be formed with/without the breaking of the H-bonds present in the pure liquids.

It is well known that the primary amines are self-associated through the formation of H-bonds and exert stronger intermolecular forces than the tertiary amines. It would be advantageous to investigate and interpret the excess molar volume $V^E$, the viscosity deviation $\Delta \eta$ and the excess Gibbs energy of activation $\Delta G^{*E}$ results when a tertiary amine is mixed with an 1-alkanol molecule, because in contradiction to

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primary amines, the tertiary ones cannot from multimers of type $A_iB_j$ [5]. If they can form mixed multimers with 1-alkanols, these species should be of the types $A_iB$ (where the value of $i$ is 1–3, etc.) only. Therefore, in this paper we extend our studies to the binary mixtures formed from series of 1-alkanols with tri-$n$-butylamine. This study will shed some more light on the formation of mixed species and their influence on the excess properties of the mixtures. Furthermore, these data will be very useful to examine the applicability of the ERAS model [6,7], which is particularly suitable to separate excess properties into physical and chemical contributions in mixtures formed from associating components.

## 2. Experiments

### 2.1. Method

Densities $\rho$ at 303.15 and 313.15 K were measured with an Anton Paar vibrating-tube digital densimeter (model DMA 60/602) with a thermostated bath controlled to $\pm 0.01$ K. Viscosities $\eta$ at the same temperatures were measured with a modified calibrated suspended level Ubbelohde viscometer. The details of the methods and techniques used to determine $\rho$ and $\eta$ have been described previously [1,8].

The mixtures were prepared by mixing known masses of pure liquids in air tight, narrow-mouth ground stoppered bottles taking precautions to minimize evaporation losses. All the mass measurements were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg. The possible error in the mole fraction is estimated to be $< 1 \times 10^{-4}$. The error in $\eta$ and $\rho$ was $< 2 \times 10^{-3}$ mPa s and $2 \times 10^{-5}$ g cm$^{-3}$, respectively.

### 2.2. Source and purity of samples

The source and purification process of pure liquids 1-propanol, 1-butanol, 1-pentanol, 1-heptanol, 1-octanol and 1-decanol have been described in our earlier paper [1]. Tri-$n$-butylamine (E. Merck, AR) was stored over sodium hydroxide pellets for several days and fractionally distilled twice [9]. The purity of the liquid samples was checked by gas–liquid chromatography and boiling point measurements. The estimated purity of all the samples was better than 99.5% for 1-alkanols and 99.9% for tri-$n$-butylamine. The measured values of the densities and the viscosities were in agreement with the literature values [10–20] (Table 1) within experimental uncertainties.

Table 1
Comparison of densities and viscosities of pure liquids at 303.15 K

| Liquids | Density (g cm$^{-3}$) | | Viscosity (mPa s) | |
|---|---|---|---|---|
| | Expt | Lit | Expt | Lit |
| 1-Propanol | 0.79584 | 0.79561 [10], 0.79588 [11] | 1.7843 | 1.786 [12] |
| 1-Butanol | 0.80194 | 0.80193 [11], 0.80195 [13] | 2.2833 | 2.282 [14], 2.271 [12] |
| 1-Pentanol | 0.80736 | 0.80729 [11], 0.80740 [13] | 2.8315 | 2.833 [15], 2.844 [12] |
| 1-Heptanol | 0.81530 | 0.81550 [12], 0.8157 [13] | 4.7853 | 4.771 [15], 4.814 [16] |
| 1-Octanol | 0.81831 | 0.81830 [12], 0.81906 [11] | 6.1023 | 6.125 [12] |
| 1-Decanol | 0.82288 | 0.82285 [10], 0.82290 [11] | 8.8347 | |
| Tri-$n$-butyl amine | 0.77037 | 0.7703 [17], 0.7706 [18] | 1.1670 | 1.166 [19], 1.17 [20] |

Table 2
Densities, viscosities, excess molar volumes and Gibbs energy of activation of viscous flow for 1-alkanol (A) + tri-*n*-butylamine (B) at 303.15 and 313.15 K

| $x_B$ | 303.15 K | | | | 313.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| | $\rho$ (g cm$^{-3}$) | $\eta$ (mPa s) | $V^E$ (cm$^3$ mol$^{-1}$) | $\Delta G^{*E}$ (J mol$^{-1}$) | $\rho$ (g cm$^{-3}$) | $\eta$ (mPa s) | $V^E$ (cm$^3$ mol$^{-1}$) | $G^{*E}$ (J mol$^{-1}$) |
| 1-Propanol + tri-*n*-butylamine | | | | | | | | |
| 0.0000 | 0.79584 | 1.7843 | | | 0.78747 | 1.3970 | | |
| 0.0929 | 0.79216 | 1.7498 | −0.297 | 236 | 0.78386 | 1.3642 | −0.269 | 212 |
| 0.1877 | 0.78894 | 1.7118 | −0.527 | 402 | 0.78072 | 1.3282 | −0.473 | 349 |
| 0.2897 | 0.78583 | 1.6594 | −0.688 | 503 | 0.77783 | 1.2886 | −0.629 | 432 |
| 0.3991 | 0.78288 | 1.6054 | −0.783 | 562 | 0.77502 | 1.2450 | −0.711 | 465 |
| 0.5176 | 0.77987 | 1.5288 | −0.771 | 548 | 0.77214 | 1.2027 | −0.685 | 461 |
| 0.6160 | 0.77755 | 1.4622 | −0.686 | 498 | 0.76997 | 1.1529 | −0.602 | 393 |
| 0.7064 | 0.77553 | 1.3921 | −0.550 | 413 | 0.76814 | 1.1204 | −0.486 | 338 |
| 0.8055 | 0.77354 | 1.3070 | −0.371 | 279 | 0.76630 | 1.0806 | −0.320 | 247 |
| 0.8864 | 0.77213 | 1.2518 | −0.223 | 179 | 0.76500 | 1.0463 | −0.184 | 153 |
| 1.0000 | 0.77037 | 1.1670 | | | 0.76344 | 0.9974 | | |
| 1-Butanol + tri-*n*-butylamine | | | | | | | | |
| 0.0000 | 0.80194 | 2.2833 | | | 0.79405 | 1.8170 | | |
| 0.0942 | 0.79775 | 2.1594 | −0.338 | 136 | 0.79004 | 1.7101 | −0.340 | 112 |
| 0.1897 | 0.79391 | 2.0282 | −0.596 | 219 | 0.78620 | 1.6083 | −0.577 | 184 |
| 0.3149 | 0.78935 | 1.8769 | −0.812 | 293 | 0.78155 | 1.4812 | −0.747 | 224 |
| 0.4192 | 0.78586 | 1.7656 | −0.890 | 329 | 0.77803 | 1.3932 | −0.790 | 243 |
| 0.5187 | 0.78275 | 1.6499 | −0.883 | 318 | 0.77498 | 1.3115 | −0.766 | 232 |
| 0.6180 | 0.77981 | 1.5425 | −0.798 | 290 | 0.77216 | 1.2314 | −0.680 | 195 |
| 0.7149 | 0.77708 | 1.4478 | −0.642 | 253 | 0.76958 | 1.1536 | −0.534 | 133 |
| 0.8007 | 0.77483 | 1.3648 | −0.464 | 202 | 0.76753 | 1.1022 | −0.388 | 99 |
| 0.9031 | 0.77243 | 1.2561 | −0.237 | 97 | 0.76532 | 1.0474 | −0.193 | 54 |
| 1.0000 | 0.77037 | 1.1670 | | | 0.76346 | 0.9974 | | |
| 1-Pentanol + tri-*n*-butylamine | | | | | | | | |
| 0.0000 | 0.80736 | 2.8315 | | | 0.79987 | 2.3443 | | |
| 0.0945 | 0.80291 | 2.6218 | −0.374 | 92 | 0.79541 | 2.1217 | −0.363 | 28 |
| 0.1881 | 0.79877 | 2.4054 | −0.656 | 136 | 0.79114 | 1.9095 | −0.612 | 16 |
| 0.2845 | 0.79471 | 2.1796 | −0.853 | 137 | 0.78694 | 1.7139 | −0.767 | −14 |
| 0.3843 | 0.79075 | 1.9614 | −0.971 | 110 | 0.78294 | 1.5510 | −0.857 | −35 |
| 0.4829 | 0.78705 | 1.7858 | −1.005 | 95 | 0.77921 | 1.4151 | −0.862 | −53 |
| 0.6148 | 0.78232 | 1.5814 | −0.913 | 64 | 0.77456 | 1.2661 | −0.756 | −69 |
| 0.7041 | 0.77926 | 1.4584 | −0.768 | 36 | 0.77162 | 1.1881 | −0.618 | −61 |
| 0.7980 | 0.77621 | 1.3646 | −0.559 | 43 | 0.76872 | 1.1181 | −0.429 | −46 |
| 0.8912 | 0.77334 | 1.2621 | −0.301 | 13 | 0.76609 | 1.0540 | −0.220 | −36 |
| 1.0000 | 0.77037 | 1.1670 | | | 0.76344 | 0.9974 | | |
| 1-Heptanol + tri-*n*-butylamine | | | | | | | | |
| 0.0000 | 0.81530 | 4.7853 | | | 0.80897 | 3.5786 | | |
| 0.1067 | 0.81014 | 4.1333 | −0.449 | 40 | 0.80325 | 3.0326 | −0.370 | −43 |
| 0.1877 | 0.80636 | 3.6774 | −0.732 | 50 | 0.79915 | 2.6899 | −0.603 | −67 |
| 0.2841 | 0.80180 | 3.1783 | −0.961 | 39 | 0.79446 | 2.3551 | −0.815 | −78 |
| 0.4197 | 0.79553 | 2.5585 | −1.138 | −15 | 0.78811 | 1.9563 | −0.983 | −101 |
| 0.5183 | 0.79094 | 2.1907 | −1.129 | −55 | 0.78357 | 1.7090 | −0.990 | −125 |

Table 2 (*Continued*)

| $x_B$ | 303.15 K | | | | 313.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| | $\rho$ (g cm$^{-3}$) | $\eta$ (mPa s) | $V^E$ (cm$^3$ mol$^{-1}$) | $\Delta G^{*E}$ (J mol$^{-1}$) | $\rho$ (g cm$^{-3}$) | $\eta$ (mPa s) | $V^E$ (cm$^3$ mol$^{-1}$) | $G^{*E}$ (J mol$^{-1}$) |
| 0.6190 | 0.78637 | 1.8812 | −1.032 | −87 | 0.77897 | 1.4968 | −0.888 | −141 |
| 0.7191 | 0.78192 | 1.6444 | −0.847 | −80 | 0.77452 | 1.3299 | −0.703 | −127 |
| 0.8008 | 0.77835 | 1.4818 | −0.628 | −64 | 0.77103 | 1.2168 | −0.506 | −99 |
| 0.8900 | 0.77466 | 1.3285 | −0.363 | −38 | 0.76744 | 1.1002 | −0.271 | −82 |
| 1.0000 | 0.77037 | 1.1670 | | | 0.76344 | 0.9974 | | |
| 1-Octanol + tri-*n*-butylamine | | | | | | | | |
| 0.0000 | 0.81831 | 6.1023 | | | 0.81188 | 4.4132 | | |
| 0.0904 | 0.81415 | 5.2871 | −0.430 | 28 | 0.80743 | 3.7670 | −0.392 | −47 |
| 0.1906 | 0.80936 | 4.4638 | −0.785 | 31 | 0.80238 | 3.1715 | −0.709 | −95 |
| 0.2864 | 0.80475 | 3.7648 | −1.030 | 8 | 0.79753 | 2.6978 | −0.913 | −137 |
| 0.4192 | 0.79820 | 2.9348 | −1.188 | −59 | 0.79082 | 2.1852 | −1.043 | −165 |
| 0.5184 | 0.79333 | 2.4295 | −1.196 | −121 | 0.78584 | 1.8724 | −1.028 | −183 |
| 0.6196 | 0.78833 | 2.0248 | −1.094 | −161 | 0.78082 | 1.6193 | −0.921 | −171 |
| 0.7144 | 0.78370 | 1.7230 | −0.916 | −178 | 0.77625 | 1.4236 | −0.759 | −145 |
| 0.8124 | 0.77895 | 1.4875 | −0.644 | −147 | 0.77159 | 1.2505 | −0.512 | −112 |
| 0.8987 | 0.77493 | 1.3300 | −0.370 | −79 | 0.76766 | 1.1283 | −0.263 | −55 |
| 1.0000 | 0.77037 | 1.1670 | | | 0.76344 | 0.9974 | | |
| 1-Decanol + tri-n-butylamine | | | | | | | | |
| 0.0000 | 0.82288 | 8.8347 | | | 0.81606 | 6.9555 | | |
| 0.0952 | 0.81886 | 7.1923 | −0.502 | −33 | 0.81163 | 5.6588 | −0.414 | −55 |
| 0.1901 | 0.81448 | 5.8452 | −0.870 | −71 | 0.80701 | 4.5957 | −0.730 | −116 |
| 0.2866 | 0.80970 | 4.7535 | −1.116 | −100 | 0.80216 | 3.7208 | −0.961 | −177 |
| 0.3816 | 0.80484 | 3.8735 | −1.266 | −131 | 0.79728 | 3.0260 | −1.107 | −235 |
| 0.5195 | 0.79744 | 2.9105 | −1.294 | −147 | 0.78990 | 2.2880 | −1.138 | −265 |
| 0.6185 | 0.79194 | 2.3580 | −1.186 | −172 | 0.78446 | 1.8923 | −1.043 | −258 |
| 0.7198 | 0.78622 | 1.9276 | −0.978 | −163 | 0.77874 | 1.5860 | −0.829 | −205 |
| 0.8029 | 0.78150 | 1.6577 | −0.744 | −119 | 0.77408 | 1.3876 | −0.606 | −133 |
| 0.9006 | 0.77595 | 1.3782 | −0.402 | −86 | 0.76863 | 1.1749 | −0.287 | −73 |
| 1.0000 | 0.77037 | 1.1670 | | | 0.76344 | 0.9974 | | |

## 3. Results

The measured $\eta$ and $\rho$ for pure liquids and binary mixtures at a number of mole fractions at 303.15 and 313.15 K are given in Table 2.

The excess molar volumes $V^E$ were calculated from the molar masses $M_i$ and the densities of the pure liquids and the mixtures as

$$V^E = x_A M_A \left( \frac{1}{\rho} - \frac{1}{\rho_A} \right) + x_B M_B \left( \frac{1}{\rho} - \frac{1}{\rho_B} \right) \tag{1}$$

The viscosity deviations from the linear dependence on mole fraction were calculated by

$$\Delta \eta = \eta - (x_A \eta_A + x_B \eta_B) \tag{2}$$

Table 3
Coefficients $A_i$ and standard deviations $\sigma$ of Eq. (4)

| Property | Temperature (K) | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| 1-Propanol + tri-*n*-butylamine | | | | | | |
| $V^E$ (cm$^3$ mol$^{-1}$) | 303.15 | −3.0965 | 0.8529 | 0.4308 | | 0.0061 |
| | 313.15 | −2.7785 | 0.8741 | 0.4821 | | 0.0041 |
| $\Delta\eta$ (mPa s) | 303.15 | 0.2594 | −0.0937 | −0.1008 | | 0.0034 |
| | 313.15 | 0.0298 | −0.0094 | 0.0192 | | 0.0029 |
| $\Delta G^{*E}$ (J mol$^{-1}$) | 303.15 | 2211.0 | −637.4 | 85.4 | | 7.7 |
| | 313.15 | 1817.5 | −592.9 | 303.2 | | 6.4 |
| 1-Butanol + tri-*n*-butylamine | | | | | | |
| $V^E$ (cm$^3$ mol$^{-1}$) | 303.15 | −3.5471 | 0.7734 | 0.3515 | | 0.0055 |
| | 313.15 | −3.0906 | 1.0128 | 0.0052 | 0.1420 | 0.0047 |
| $\Delta\eta$ (mPa s) | 303.15 | −0.2192 | 0.0519 | −0.0178 | | 0.0047 |
| | 313.15 | −0.3433 | −0.0047 | −0.0136 | | 0.0043 |
| $\Delta G^{*E}$ (J mol$^{-1}$) | 303.15 | 1295.3 | −230.9 | 96.2 | | 7.9 |
| | 313.15 | 903.7 | −446.0 | 67.2 | | 9.0 |
| 1-Pentanol + tri-*n*-butylamine | | | | | | |
| $V^E$ (cm$^3$ mol$^{-1}$) | 303.15 | −4.0107 | 0.5281 | 0.4464 | 0.4345 | 0.0029 |
| | 313.15 | −3.4179 | 0.8833 | 0.3047 | 0.5760 | 0.0022 |
| $\Delta\eta$ (mPa s) | 303.15 | −0.9760 | −0.0187 | 0.3718 | −0.2221 | 0.0053 |
| | 313.15 | −1.1192 | 0.3025 | 0.1465 | −0.2796 | 0.0028 |
| $\Delta G^{*E}$ (J mol$^{-1}$) | 303.15 | 361.4 | −553.2 | 423.7 | | 8.4 |
| | 313.15 | −235.0 | −371.9 | 338.6 | | 7.9 |
| 1-Heptanol + tri-*n*-butylamine | | | | | | |
| $V^E$ (cm$^3$ mol$^{-1}$) | 303.15 | −4.5671 | 0.6646 | 0.5715 | | 0.0051 |
| | 313.15 | −3.9636 | 0.5583 | 1.0643 | 0.2615 | 0.0038 |
| $\Delta\eta$ (mPa s) | 303.15 | −2.8726 | 0.2289 | 0.4710 | | 0.0050 |
| | 313.15 | −2.1321 | 0.5229 | −0.3239 | 0.1990 | 0.0056 |
| $\Delta G^{*E}$ (J mol$^{-1}$) | 303.15 | −190.9 | −581.3 | 357.4 | | 9.3 |
| | 313.15 | −472.3 | −233.6 | −258.1 | | 8.7 |
| 1-Octanol + tri-*n*-butylamine | | | | | | |
| $V^E$ (cm$^3$ mol$^{-1}$) | 303.15 | −4.8010 | 0.6020 | 0.2782 | 0.1980 | 0.0046 |
| | 313.15 | −4.1660 | 0.7760 | 0.5251 | 0.5884 | 0.0058 |
| $\Delta\eta$ (mPa s) | 303.15 | −4.4641 | 0.3653 | 0.5753 | 0.2019 | 0.0025 |
| | 313.15 | −3.1155 | 1.0580 | −0.1709 | | 0.0029 |
| $\Delta G^{*E}$ (J mol$^{-1}$) | 303.15 | −452.1 | 1189.2 | 265.9 | 664.7 | 5.0 |
| | 313.15 | −722.9 | −49.6 | 170.4 | | 4.6 |
| 1-Decanol + tri-*n*-butylamine | | | | | | |
| $V^E$ (cm$^3$ mol$^{-1}$) | 303.15 | −5.1931 | 0.6745 | 0.0691 | 0.2464 | 0.0040 |
| | 313.15 | −4.5963 | 0.5009 | 0.9093 | 0.7675 | 0.0045 |

Table 3 (*Continued*)

| Property | Temperature (K) | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| $\Delta\eta$ (mPa s) | 303.15 | −7.9291 | 2.7689 | −0.6736 | −0.0003 | 0.0092 |
| | 313.15 | −6.3990 | 2.4981 | −0.1968 | −0.1729 | 0.0046 |
| $\Delta G^{*E}$ (J mol$^{-1}$) | 303.15 | −614.5 | −328.1 | −83.3 | | 8.4 |
| | 313.15 | −1052.0 | 112.7 | 533.0 | | 8.0 |

On the basis of the theory of absolute reaction rates [21], the excess Gibbs energy of activation $\Delta G^{*E}$ of viscous flow were calculated from

$$\frac{\Delta G^{*E}}{RT} = \ln\left(\frac{\eta V}{\eta_B V_B}\right) - x_A \ln\left(\frac{\eta_A V_A}{\eta_B V_B}\right) \tag{3}$$

$V^E$ and $\Delta G^{*E}$ data are included in Table 2. The estimated accuracy of $V^E$ and $\Delta G^{*E}$ is about 0.005 cm$^3$ mol$^{-1}$ and 15 J mol$^{-1}$, respectively.

The values of $V^E$, $\Delta\eta$, and $\Delta G^{*E}$ for each mixture have been fitted to the Redlich–Kister polynomial equation

$$Y^E = x_A(1 - x_A)\sum_{i=0}^{m} A_i(1 - 2x_A)^i \tag{4}$$

The coefficients $A_i$ obtained from a least squares fit with equal weights assigned to each point are given in Table 3 together with the standard deviations $\sigma$.

## 4. Correlating equations

Several semi-empirical relations have been proposed to correlate the dynamic viscosity $\eta$ of liquid mixtures in terms of pure-component data [22,23]. We have examined equations proposed by Grunberg and Nissan [24], Tamura and Kurata [25], Hind et al. [26], Katti and Chaudhri [27], McAllister [28], Heric [29] and Auslaender [30]. These equations are presented as Eqs. (6)–(12) in our previous paper [3].

The correlating ability of each of the Eqs. (6)–(12) in [3], was tested by calculating the standard percentage deviations $\sigma(\%)$ between the experimental and the calculated viscosity as

$$\sigma\% = \left[\frac{1}{n - k}\sum\left\{\frac{100(\eta_{exp} - \eta_{cal})}{\eta_{exp}}\right\}^2\right]^{1/2} \tag{5}$$

where $n$ represents the number of data points and $k$ the number of numerical coefficients in the respective equations. The results of correlating equations (Eqs. (6)–(12) in [3]) are compiled in Tables 4 and 5. Table 4 lists the results of (Eqs. (6)–(12) in [3]) containing single-adjustable parameter. The results of the two-parameter McAllister equation ((10) in [3]) and the Heric equation ((11) from [3]) and of three-parameter Auslaender equation ((12) from [3]) are summarized in Table 5. The values of the different parameters and the percentage standard deviations $\sigma(\%)$ listed in Tables 4 and 5 were obtained from the experimental viscosity data with the method of least squares, with equal weights assigned to each point.

Table 4
Values of the parameters in Eqs. (6)–(9) from [3]and standard percentage deviations in correlating viscocities of 1-alkanol + tri-*n*-butylamine

| Temperature (K) | Eq. (6) | | Eq. (7) | | Eq. (8) | | Eq. (9) | |
|---|---|---|---|---|---|---|---|---|
| | $G_{12}$ (mPa s) | $\sigma$ (%) | $C$ (mPa s) | $\sigma$ (%) | $\eta_{12}$ | $\sigma$ (%) | $W_{\text{vis}}/RT$ | $\sigma$ (%) |
| 1-Propanol + tri-*n*-butylamine | | | | | | | | |
| 303.15 | 0.24 | 0.42 | 2.05 | 0.54 | 1.59 | 0.64 | 0.89 | 1.93 |
| 313.15 | 0.09 | 0.22 | 1.55 | 0.22 | 1.21 | 0.23 | 0.73 | 1.85 |
| 1-Butanol + tri-*n*-butylamine | | | | | | | | |
| 303.15 | 0.09 | 0.44 | 2.08 | 0.28 | 1.61 | 0.41 | 0.52 | 0.66 |
| 313.15 | −0.08 | 0.52 | 1.58 | 1.06 | 1.23 | 0.32 | 0.35 | 1.38 |
| 1-Pentanol + tri-*n*-butylamine | | | | | | | | |
| 303.15 | −0.10 | 1.36 | 2.02 | 2.05 | 1.56 | 1.02 | 0.19 | 1.87 |
| 313.15 | −0.34 | 0.69 | 1.51 | 1.26 | 1.13 | 1.31 | −0.05 | 1.15 |
| 1-Heptanol + tri-*n*-butylamine | | | | | | | | |
| 303.15 | −0.15 | 1.99 | 2.14 | 2.00 | 1.60 | 1.48 | −0.04 | 2.10 |
| 313.15 | −0.33 | 0.76 | 1.58 | 0.42 | 1.18 | 2.99 | −0.21 | 0.84 |
| 1-Octanol + tri-*n*-butylamine | | | | | | | | |
| 303.15 | −0.22 | 2.99 | 2.04 | 1.88 | 1.49 | 2.18 | −0.16 | 3.01 |
| 313.15 | −0.32 | 0.34 | 1.54 | 1.74 | 1.13 | 4.80 | −0.26 | 0.33 |
| 1-Decanol + tri-*n*-butylamine | | | | | | | | |
| 303.15 | −0.25 | 1.07 | 1.42 | 6.02 | 0.95 | 9.41 | −0.25 | 1.04 |
| 313.15 | −0.35 | 1.05 | 1.13 | 6.84 | 0.75 | 10.11 | −0.35 | 1.00 |

## 5. Discussion

The values of $\sigma$ in the Tables 4 and 5 are in the range from 0.22 to 10.11% for single-parameter Eqs. (6)–(9) from [3]; and from 0.28 to 0.99% for two-parameter Eqs. (10) and (11) from [3]; and from 0.17 to 0.65% for three-parameter Eq. (12) from [3]. The average values of percentage standard deviations $\langle \sigma \% \rangle$ for Eqs. (6)–(9) with single-parameter are 0.99, 2.03, 2.91 and 1.43, respectively; and for Eqs. (10) and (11) with two-parameters $\langle \sigma \% \rangle$ is 0.55 while for the three-parameter Eq. (12) the $\langle \sigma \% \rangle$ is 0.43. On analysis of the results it was observed that the use of two-parameter Eqs. (10) and (11) reduces the $\sigma \%$ values significantly below that of single-parameter equations. In most systems the three-parameter Eq. (12) proposed by McAllister [28] gives very good results. Further study of results shows that in general the correlating ability of various equations considered here is better for 1-alkanol + tri-*n*-butylamine systems than those found for 1-alkanol + primary amine [1,2] and 1-alkanol + secondary amine [3] systems.

We have calculated the $\Delta \eta$, $V^{\text{E}}$, and $\Delta G^{*\text{E}}$ at 303.15 and 313.15 K, but graphically the results are shown only at 303.15 K, since for the other temperature the curves are similar. Fig. 1 reveals that the viscosities exhibit negative deviations from linear dependence on the mole fraction over the entire range of composition for all the mixtures except very small positive deviations for 1-propanol + tri-*n*-butylamine system. It can be seen from Fig. 2 that the magnitude of negative deviations increases with chain length of 1-alkanol, and it decreases with rise of temperature from 303.15 to 313.15 K for 1-pentanol to 1-decanol mixtures

Table 5
Values of the parameters in Eqs. (10)–(12) from [3] and standard percentage deviations in correlating viscosities of 1-alkanol + tri-*n*-butylamine

| Temperature (K) | Eq. (10) | | | Eq. (11) | | | Eq. (12) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Z_{AB}$ | $Z_{BA}$ | $\sigma$ (%) | $\alpha_{AB}$ | $\alpha_{BA}$ | $\sigma$ (%) | $B_{AB}$ | $A_{BA}$ | $B_{BA}$ | $\sigma$ (%) |
| 1-Propanol + tri-*n*-butylamine | | | | | | | | | | |
| 303.15 | 1.89 | 2.47 | 0.28 | 0.89 | 0.25 | 0.28 | 0.52 | 0.95 | 1.38 | 0.53 |
| 313.15 | 1.51 | 1.90 | 0.55 | 0.73 | 0.23 | 0.55 | −0.16 | −0.18 | −6.15 | 0.28 |
| 1-Butanol + tri-*n*-butylamine | | | | | | | | | | |
| 303.15 | 1.99 | 2.56 | 0.35 | 0.52 | 0.09 | 0.35 | −0.31 | −0.25 | −3.25 | 0.39 |
| 313.15 | 1.54 | 2.05 | 0.30 | 0.35 | 0.17 | 0.30 | 0.40 | 0.29 | 2.11 | 0.49 |
| 1-Pentanol + tri-*n*-butylamine | | | | | | | | | | |
| 303.15 | 1.87 | 2.85 | 0.87 | 0.19 | 0.22 | 0.87 | 0.23 | 0.19 | 2.52 | 0.38 |
| 313.15 | 1.51 | 2.16 | 0.64 | −0.05 | 0.15 | 0.64 | 0.27 | 0.16 | 2.33 | 0.17 |
| 1-Heptanol + tri-*n*-butylamine | | | | | | | | | | |
| 303.15 | 2.13 | 3.89 | 0.75 | −0.04 | 0.23 | 0.75 | 0.58 | 0.34 | 1.03 | 0.55 |
| 313.15 | 1.74 | 2.76 | 0.49 | −0.21 | 0.08 | 0.49 | 1.69 | 0.77 | 0.44 | 0.49 |
| 1-Octanol + tri-*n*-butylamine | | | | | | | | | | |
| 303.15 | 2.15 | 4.61 | 0.65 | −0.15 | 0.35 | 0.65 | 0.79 | 0.42 | 0.62 | 0.65 |
| 313.15 | 1.89 | 3.07 | 0.29 | −0.26 | 0.02 | 0.29 | 0.52 | 0.23 | 1.46 | 0.21 |
| 1-Decanol + tri-*n*-butylamine | | | | | | | | | | |
| 303.15 | 2.55 | 5.34 | 0.34 | −0.25 | 0.13 | 0.34 | 0.81 | 0.33 | 0.76 | 0.35 |
| 313.15 | 2.14 | 4.11 | 0.99 | −0.35 | 0.04 | 0.99 | 0.36 | 0.15 | 1.80 | 0.62 |

while opposite is the case for other two mixtures of 1-propanol and 1-butanol. The observed positive deviations over the entire range of composition for 1-propanol + tri-*n*-butylamine support predominance of specific interactions [31]. But for the rest of the mixtures observed negative deviations which regularly increase as the size or viscosity of 1-alkanol is increased can be explained by the fact that the average degree of association in the 1-alkanol (1-butanol to 1-decanol through 1-pentanol, 1-heptanol, 1-octanol) + tri-*n*-butylamine mixture decreases on proceeding from the 1-alkanol towards the amine as composition is varied [32]. Alkanol molecules self-associate strongly (OH · · · OH interaction) while the triamine molecules associate through dipole interactions rather marginally, and this has a dramatic influence on the thermo-physical properties studied.

Fig. 3 shows that the $V^E$ are large and negative for all the six 1-alkanol + tri-*n*-butylamine mixtures over entire range of compositions. The magnitude of negative values of $V^E$ increases with increase of chain length of 1-alkanol and decreases with rise of temperature from 303.15 to 313.15 K (Fig. 4). Large negative $V^E$ for 1-alkanol + triethylamine (methanol, ethanol, 1-propanol and 1-butanol −2.23 to −1.92 cm$^3$ mol$^{-1}$ for $x_B = 0.5$ at 298.15 K [33–35]), and for 1-propanol + tripropylamine (−0.846 cm$^3$ mol$^{-1}$ for $x_B = 0.5$ and at 298.15 K [36]) have also been observed.

The values of $\sum_{i=0}^{n} A_i$ and $\sum_{i=0}^{n} A_i(-1)^i$ of Eq. (4) represent the limiting values of excess partial molar volumes of both alkanol and amine equivalent to $V_A^{E,\infty}(= \bar{V}_A - V_A^0)$ and $V_B^{E,\infty}(= \bar{V}_B - V_B^0)$, the difference between the partial molar volume of component A or B at infinite dilution and the molar volume of the pure
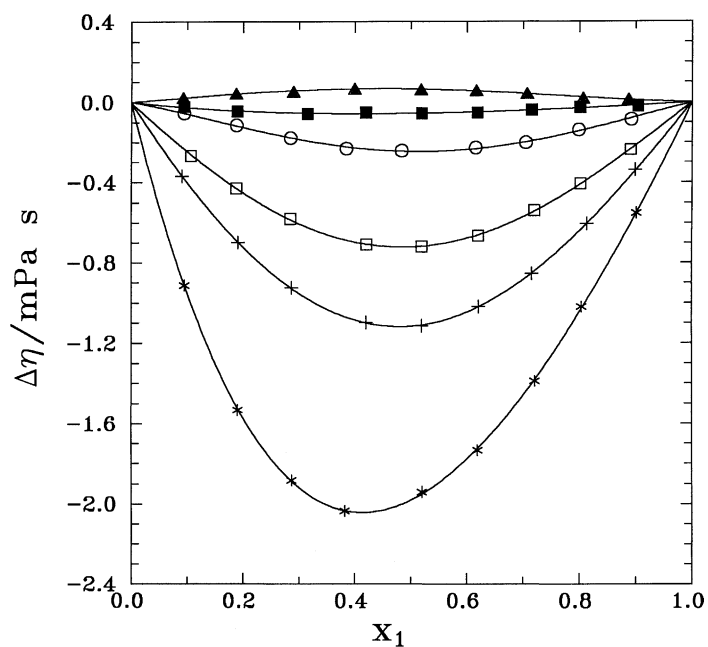
Fig. 1. Viscosity deviations $\Delta\eta$ in 1-alkanol + tri-$n$-butylamine at 303.15 K. Experimental points: 1-alkanol, $C_3H_7OH$ (▲); $C_4H_9OH$ (■); $C_5H_{11}OH$ (○); $C_7H_{15}OH$ (□); $C_8H_{17}OH$ (+); $C_{10}H_{21}OH$ (✷).
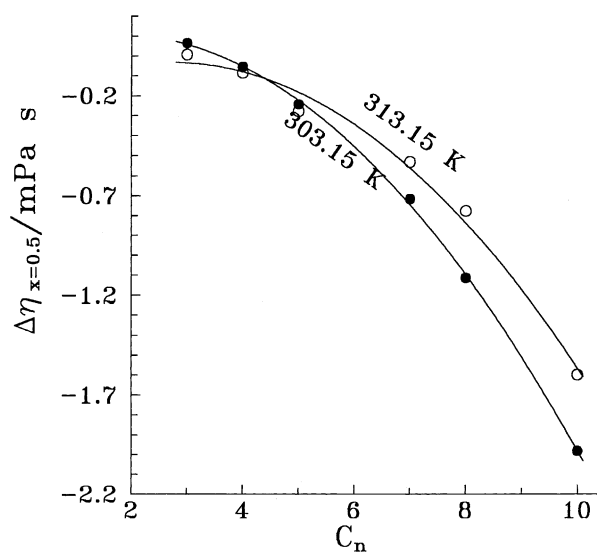


Fig. 2. Equimolar viscosity deviations $\Delta\eta$ as a function of number of carbon atoms ($C_n$) in 1-alkanols, 303.15 K (●) and 313.15 K (○).
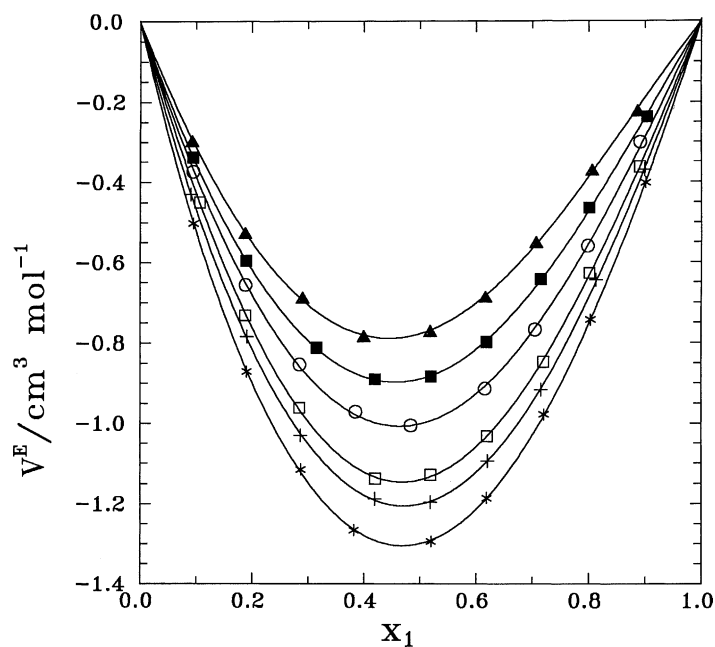
Fig. 3. Excess molar volumes $V^E$ of 1-alkanol + tri-$n$-butylamine at 303.15 K. Experimental points: 1-alkanol, $C_3H_7OH$ (▲); $C_4H_9OH$ (■); $C_5H_{11}OH$ (○); $C_7H_{15}OH$ (□); $C_8H_{17}OH$ (+); $C_{10}H_{21}OH$ (✳).
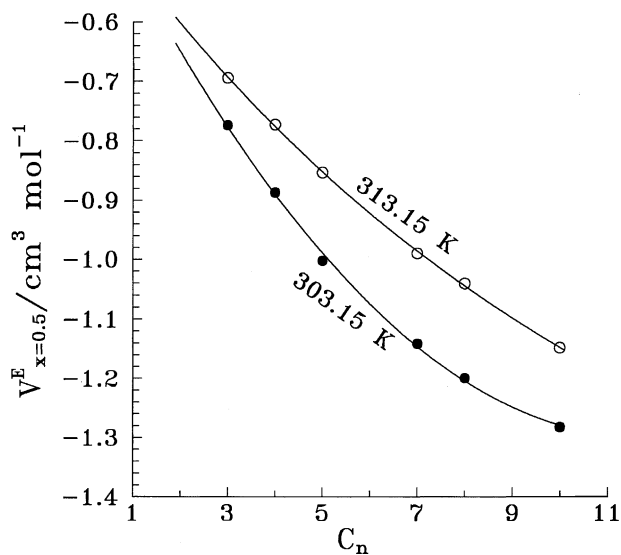


Fig. 4. Equimolar excess molar volumes as a function of number of carbon atoms ($C_n$) in 1-alkanols, 303.15 K (●) and 313.15 K (○).
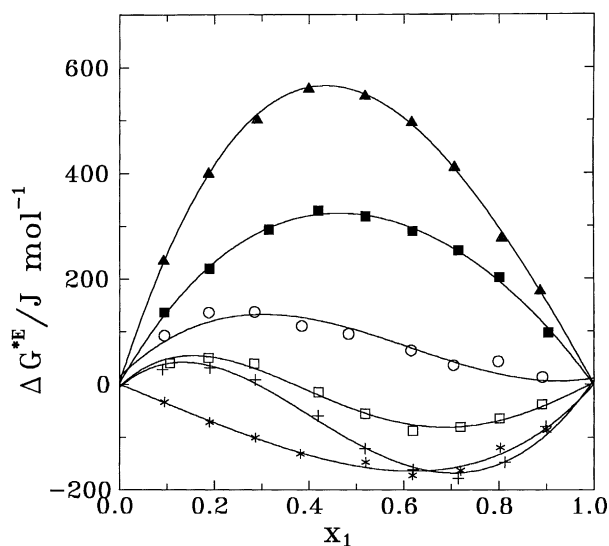
Fig. 5. Excess Gibbs energy of activation $\Delta G^{*E}$ of viscous flow for 1-alkanol + tri-$n$-butylamine at 303.15 K. Experimental points: 1-alkanol, $C_3H_7OH$ (▲); $C_4H_9OH$(■); $C_5H_{11}OH$ (○); $C_7H_{15}OH$ (□); $C_8H_{17}OH$ (+); $C_{10}H_{21}OH$ (✳).

liquid [34]. The limiting values of $V_i^{E,\infty}$ of tri-$n$-butylamine $V_B^{E,\infty}$ vary from $-3.52$ to $-6.04$ cm$^3$ mol$^{-1}$ in 1-propanol to 1-decanol and for 1-alkanols these values are in the range from $-1.81$ to $-4.20$ cm$^3$ mol$^{-1}$ in tri-$n$-butylamine. Somewhat large negative values were observed in methanol + triethylamine [34]. The large negative contribution to $V_i^{E,\infty}$ for both amine and 1-alkanol in the present mixtures clearly suggests the dominance of strong specific interactions between components and the free volume effect when mixture is formed.

The values of $\Delta G^{*E}$ are positive for 1-propanol + tri-$n$-butylamine which gradually decrease with chain length of 1-alkanol (Fig. 5). Systems involving 1-pentanol, 1-heptanol and 1-octanol have both small positive as well as small negative values of $\Delta G^{*E}$, depending upon the composition and the temperature of the mixtures. For these mixtures as the composition of amine is increased, the $\Delta G^{*E}$ values change the sign from positive to negative. For 1-decanol + tri-$n$-butylamine, $\Delta G^{*E}$ are negative at both the temperatures and at all the compositions. With rise in temperature the values of $\Delta G^{*E}$ decrease.

Like primary and secondary amines [1–3], the present large and negative $V^E$ results can be interpreted qualitatively by taking into account the fact that several expansion and contraction processes proceed simultaneously when alkanol–amine mixtures are formed. The following effects were considered: (i) expansion due to depolymerization of alcohol and disruption of dipolar order of triamine by one another; (ii) contraction due to free volume difference of unlike molecules; and (iii) contraction due to mutual association through hydrogen bond formation between alcohol and triamine through ROH$\cdots$ NR$_3$.

The large positive $V^E$ observed in case of ROH + $C_6H_{12}$ [37,38] and $R_3N$ + $C_6H_{12}$ [39,40] mixtures, as a result of disruption of the self-association of 1-alkanol and amine by the addition of inert globular hydrocarbon molecules, suggests positive contribution to $V^E$ due to effect: (i) the estimated free volume contribution (ii) to $V^E$ as per the Prigogine–Flory–Patterson theory [41] ranges from $-0.002$ cm$^3$ mol$^{-1}$ for

1-propanol + tri-*n*-butylamine to $-0.087 \, \text{cm}^3 \, \text{mol}^{-1}$ for 1-decanol + tri-*n*-butylamine. Thus, the observed very large negative values of $V^E$ can be accounted only by considering predominance of the formation of OH $\cdots$ N, bonds over the rupture of the OH $\cdots$ OH bonds and disruption of dipolar order present in pure triamine. It has been shown by Allen [42] that bonding energies of O–H $\cdots$ O in water is about $-31 \, \text{kJ} \, \text{mol}^{-1}$, the corresponding value for the N–H $\cdots$ N bonding in ammonia is about $-16 \, \text{kJ} \, \text{mol}^{-1}$. The energies for the cross bonding O–H $\cdots$ N are $-36 \, \text{kJ} \, \text{mol}^{-1}$. This indicates the energetic superiority of the O–H $\cdots$ N structure. The existence of strong O–H $\cdots$ N bond has also been confirmed through NMR [43], IR [44] and UV [45] studies.

Furthermore, the minimum values of excess enthalpies $H^E$ for mixtures of methanol, ethanol, 1-propanol, 1-butanol, and 1-heptanol with tri-*n*-butylamine at 293.15 K are $-761$, $-238$, $-368$, $-448$ and $-519 \, \text{J} \, \text{mol}^{-1}$, respectively [5]. Ratkovics and Salamon [5] concluded from $H^E$ results that tri-*n*-butylamine forms an $A_iB$ type mixed multimers which contains several alcohol molecules in addition to AB type complexes. However, it is seen that $H^E$ for 1-alkanol + butylamine from $-3815$ to $-2705 \, \text{J} \, \text{mol}^{-1}$ [46,47] are comparatively much large negative than those observed for 1-alkanol + tri-*n*-butylamine. Thus, specific interactions in case of tri-*n*-butylamine mixtures are comparatively very weak than those in primary amine mixtures. This is due to the fact that tri-*n*-butylamine can form fewer H-bonds with 1-alkanols through the complexes of type $A_iB$ while the primary amine can form more H-bonds through the complexes of type $A_iB_j$. Further analysis of the results on the basis of the ERAS model [6,7] will be presented in the next paper.

*List of symbols*

| | |
|---|---|
| $A_i$ | coefficients of Eq. (4) |
| AB, $A_iB$, $A_iB_j$ | mixed associates |
| $B_{AB}$, $A_{BA}$, $B_{BA}$ | binary interaction parameters of Eq. (12) in [3] |
| $C$ | adjustable parameters of Eq (7) in [3] |
| $G$ | parameter of Eq. (6) in [3] |
| $\Delta G^{*E}$ | excess Gibbs energy of activation of viscous flow |
| $H^E$ | excess enthalpy |
| $M_i$ | molar mass of component $i$ |
| $V^E$ | excess molar volumes |
| $V_i$ | molar volumes of pure component $i$ |
| $W_{vis}$ | interaction term in Eq. (9) in [3] |
| $x_A$ | mole fraction of 1-alkanol |
| $x_B$ | Mole fraction of tri-n-butylamine |
| $Z_{AB}$, $Z_{BA}$ | binary parameters of McAllister Eq. (10) in [3] |

*Greek letters*

| | |
|---|---|
| $\alpha_{AB}$, $\alpha_{BA}$ | adjustable parameters of Eq. (11) in [3] |
| $\eta$ | viscosity of mixtures |
| $\eta_A$, $\eta_B$ | viscosity of components A and B |
| $\eta_{AB}$ | parameters of Eq. (8) in [3] |
| $\Delta \eta$ | viscosity deviation |
| $\nu$ | kinematic viscosity |
| $\rho$ | density of mixture |

| $\rho_A, \rho_B$ | density of component A and B |
|---|---|
| $\sigma$ | standard deviations |
| $\sigma$ (%) | percentage standard deviations |

## References

[1] S.L. Oswal, H.S. Desai, Fluid Phase Equilib. 149 (1998) 359–376.
[2] S.L. Oswal, H.S. Desai, Fluid Phase Equilib. 161 (1999) 191–204.
[3] S.L. Oswal, H.S. Desai, Fluid Phase Equilib. 186 (2001) 81–102.
[4] F. Ratkovics, M. Laszlo, Acta Chim. Acad. Sci. Hung. 79 (4) (1973) 395–400.
[5] F. Ratkovics, T. Salamon, Acta Chim. Acad. Sci. Hung. 91 (1976) 165–173.
[6] A. Heintz, Ber. Bunsenges. Phys. Chem. 89 (1985) 172–181.
[7] H. Funke, M. Wetzel, A. Heintz, Pure Appl. Chem. 61 (1989) 1429–1439.
[8] S.G. Patel, S.L. Oswal, J. Chem. Soc. Faraday Trans. 88 (1992) 2497–2502.
[9] T.M. Letcher, J.W. Bayles, J. Chem. Eng. Data 16 (1971) 266–271.
[10] J.L. Hales, J.H. Ellender, J. Chem. Thermodyn. 8 (1976) 1177–1184.
[11] M. Diaz-Pena, G. Tardajos, J. Chem. Thermodyn. 11 (1979) 441–445.
[12] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents Physical Properties and Methods of Purification, Wiley Interscience, New York, 1986.
[13] J. Ortega, J. Chem. Eng. Data 27 (1982) 312–317.
[14] A. Janelli, A.K. Raksit, A. Sacco, Z. Naturforsch 29a (1974) 355–358.
[15] T.M. Aminabhavi, M.I. Aralaguppi, S.B. Harogoppad, R.H. Balungdi, J. Chem. Eng. Data 38 (1993) 31–39.
[16] T.M. Aminabhavi, S.K. Raikar, J. Chem. Eng. Data 38 (1993) 310–319.
[17] S.L. Oswal, R.G. Sindhe, A.T. Patel, J.P. Dave, S.G. Patel, B.M. Patel, Int. J. Thermophys. 13 (1992) 617–627.
[18] J. Timmermans, Physico Chemical Constants of Pure Organic Compounds, vols. 1–2, Elsevier, Amsterdam, 1950, 1965.
[19] C. Klofutar, S. Paljk, D. Kremser, J. Inorg. Nucl. Chem. 37 (1975) 1729–1733.
[20] F. Ratkovics, T. Salamon, L. Domonkos, Acta Chim. Acad. Sci. Hung. 83 (1974) 71–77.
[21] S. Glasstone, K.J. Laidler, H. Eyring, The Theory of Rate Process, McGraw-Hill, New York, 1941, pp. 514–516.
[22] J.B. Irving, Viscosity of liquid mixtures, NEL Report Nos. 630 and 631, National Engineering Laboratory, East Kilbride, Glasgow, 1977.
[23] W. Cao, A. Fredenslund, P. Rasmussen, Ind. Eng. Chem. Res. 31 (1992) 2603.
[24] L. Grunberg, A.H. Nissan, Nature 164 (1949) 799–800.
[25] M. Tamura, M. Kurata, Bull. Chem. Soc. Jpn. 25 (1952) 32–37.
[26] R.K. Hind, E. McLaughlin, A.R. Ubbelohde, Trans. Faraday Soc. 56 (1960) 328–334.
[27] P.K. Katti, M.M. Chaudhri, J. Chem. Eng. Data 9 (1964) 442–443.
[28] R.A. McAllister, AIChE J. 6 (1960) 427–431.
[29] E.L. Heric, J. Chem. Eng. Data 11 (1966) 66–68.
[30] G. Auslaender, Brit. Chem. Eng. 10 (1965) 196.
[31] R.J. Fort, W.R. Moore, Trans. Faraday Soc. 62 (1966) 1112–1119.
[32] F. Ratkovics, T. Salamon, L. Domonkos, Acta. Chim. Acad. Sci. Hung. 83 (1) (1974) 53–61.
[33] M. Bender, J. Hauser, A. Heintz, Ber. Buns. Phys. Chem. 95 (1991) 801–811.
[34] K. Nakanishi, H. Shairai, Bull Chem. Soc. Jpn. 43 (1970) 1634–1642.
[35] J. Copp, T.J.V. Findlay, Faraday Trans. Soc. 56 (1960) 13–22.
[36] T.M. Letcher, B.C. Bricknell, J. Chem. Eng. Data 41 (1996) 639–643.
[37] S.L. Oswal, K.D. Prajapati, J. Chem. Eng. Data 43 (1998) 367–372.
[38] J.M. Jansens, M. Rule, Can. J. Chem. Eng. 50 (1972) 591–594.
[39] T.M. Letcher, J. Chem. Thermodyn. 4 (1972) 159–173.
[40] S.L. Oswal, A.T. Patel, J. Chem. Eng. Data 39 (1994) 366–371.
[41] D. Patterson, G. Delmas, Disc. Faraday Soc. 49 (1970) 98–105.

[42] L.C. Allen, J. Am. Chem. Soc. 97 (1975) 6921–6940.
[43] P. Huyskens, T.Z. Huyskens, Bull. Soc. Chim. Belge. 69 (1960) 267–281.
[44] K. Nakanishi, S. Ichinose, H. Shirai, Ind. Eng. Chem. Fundam. 7 (1968) 381.
[45] S. Sawamura, Y. Taniguchi, K. Suzuki, Ber. Bunsenges Phys. Chem. 92 (1988) 880.
[46] J.J. Christensen, R.W. Hanks, R.M. Izatt, Handbook of Heats of Mixing, Wiley/Interscience, New York, 1982.
[47] J.J. Christensen, R.L. Rowley, R.M. Izatt, Handbook of Heats of Mixing, Supplementary Volume, Wiley/Interscience, New York, 1988.