# Excess Enthalpies and Volumes for Mixtures of (Acetonitrile + a Carboxylic Acid) at 298.15 K

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Excess molar enthalpies and excess molar volumes for mixtures of (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) at 298.15 K are presented. The excess molar enthalpy values are found to be positive for all six systems, whereas the excess molar volumes are found to be negative. The excess molar enthalpy values are correlated by the UNIQUAC and NRTL models and also by the Redlich Kister polynomial.

## Introduction

In continuation of our work on the thermodynamic effects of mixtures containing polar organic substances (Letcher and Redhi, 1991; Letcher and Domańska, 1994; Letcher et al., 1990, 1996), we have, in this work, determined the excess molar enthalpies ($H_m^E$) and excess molar volumes ($V_m^E$) of the six liquid mixtures (acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) over the whole composition range at the temperature 298.15 K. The excess enthalpy values for all of the above mixtures at 298.15 K have not been reported in the literature, whereas the excess molar volumes for three of the six systems reported here have previously been reported by Lark and Banipal (1985).

Excess enthalpy measurements have been reported on related systems. Endothermic effects were observed for (acetonitrile + ethyl ethanoate or propyl ethanoate or butyl ethanoate) by Mato et al. (1973), for (acetonitrile + 1-propanol or 2-propanol or butanol) by Nagata and Tamura (1988), and for (acetonitrile + diethyl ether or dipropyl ether or di-1-methylethyl ether or dibutyl ether or 1,1-dimethylethyl methyl ether or 1,1-dimethylpropyl methyl ether or tetrahydropyran) by Letcher and Domanska (1994) The overall endothermic effects seen in the last two mixtures are probably due to the breakdown of self-association between acetonitrile molecules and between ester molecules or between alcohol molecules.

The results obtained in this work were interpreted in terms of association of the acids, dipole−dipole interactions between heteromolecules, and the steric hindrance caused by the increased methylation. The Redlich−Kister polynomial, the NRTL model of Renon and Prausnitz (1967), and the UNIQUAC model of Abrams and Prausnitz (1975) were used to correlate the experimental data.

## Experimental Section

***Chemicals.*** The acids were obtained from Acros Chemicals, and acetic acid and 2-methylpropanoic acid had purities of >99.5 mass %, while the rest of the acids were all >99 mass % pure. The compounds were dried using activated type 4 Å molecular sieves and analyzed using the Karl Fischer technique, showing that the water content was <0.01 mass %. Acetonitrile was purchased from Aldrich Chemical Co. Analysis by GLC showed that the total mole fractions of impurities were <0.02%. The physical properties are shown in Table 1.

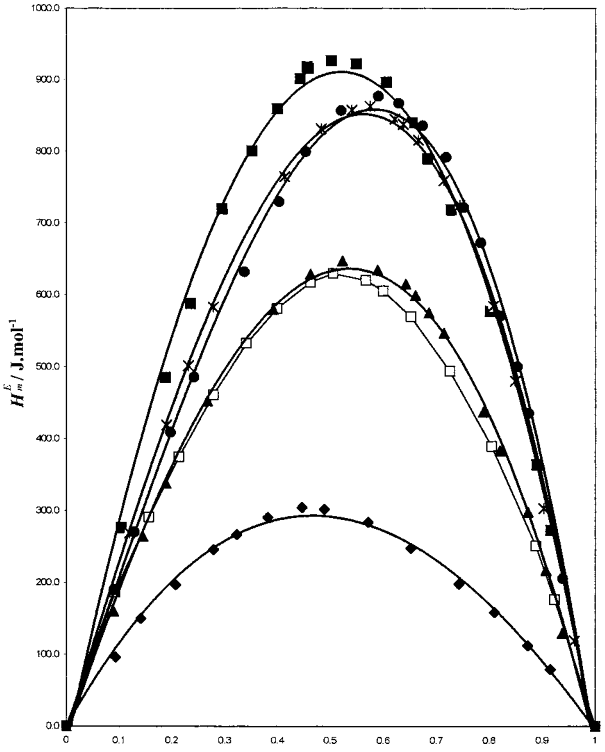

**Figure 1.** Excess molar enthalpies for the systems [acetonitrile (1) + a carboxylic acid (2)] at 298.15 K, as a function of mole fraction $x_1$: (◆) acetic acid; (□) propanoic acid; (▲) butanoic acid; (●) 3-methylbutanoic acid; (*) pentanoic acid; (■) 2-methylpropanoic acid.

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**Table 1. Physical Properties of the Pure Components at 298.15 K: Refractive Indices $n_D$ and Surface Parameter $Q$**

| component | $n_D$ |  | $Q^b$ |
|---|---|---|---|
|  | exp | lit$^a$ |  |
| acetonitrile | 1.3413 | 1.3416 | 1.724 |
| acetic acid | 1.3697 | 1.3698 | 2.072 |
| propanoic acid | 1.3846 | 1.3843 | 2.612 |
| butanoic acid | 1.3955 | 1.3958 | 3.152 |
| 2-methylpropanoic acid | 1.3913 | 1.3917 | 3.148 |
| pentanoic acid | 1.4064 | 1.4060 | 3.692 |
| 3-methylbutanoic acid | 1.4019 | 1.4022 | 3.688 |

[a] Riddick et al. (1986). [b] Gmehling et al. (1993).

**Table 2. Excess Molar Enthalpies $H^E_m$ for the Systems [Acetonitrile (1) + a Carboxylic Acid (2)] and the Deviations $\delta H^E_m$ Calculated from Eq 1 and the Parameters of Table 3 at the Experimental Temperature 298.15 K, as a Function of Mole Fraction $x_1$**

| $x_1$ | $H^E_m$/ J·mol$^{-1}$ | $\delta H^E_m$/ J·mol$^{-1}$ | $x_1$ | $H^E_m$/ J·mol$^{-1}$ | $\delta H^E_m$/ J·mol$^{-1}$ |
|---|---|---|---|---|---|
|  |  | Acetic Acid |  |  |  |
| 0.0927 | 96.2 | 0.1 | 0.4885 | 302.4 | 3.5 |
| 0.1409 | 150.1 | 6.7 | 0.5710 | 284.3 | 1.6 |
| 0.2072 | 197.3 | −3.5 | 0.6514 | 247.9 | −3.5 |
| 0.2787 | 245.9 | −3.5 | 0.7416 | 198.3 | −4.0 |
| 0.3221 | 267.1 | −4.1 | 0.8090 | 158.7 | 0.7 |
| 0.3810 | 291.2 | 0.2 | 0.8722 | 112.3 | 1.1 |
| 0.4460 | 304.7 | 4.7 | 0.9150 | 79.4 | 2.7 |
|  |  | Propanoic Acid |  |  |  |
| 0.0920 | 186.4 | 8.8 | 0.5671 | 620.1 | 3.4 |
| 0.1560 | 291.0 | 1.3 | 0.5993 | 605.9 | 0.7 |
| 0.2134 | 375.0 | −4.9 | 0.6517 | 570.0 | −3.5 |
| 0.2780 | 461.1 | −6.0 | 0.7248 | 494.5 | −8.8 |
| 0.3407 | 532.6 | −2.6 | 0.8046 | 389.9 | −3.1 |
| 0.3990 | 581.2 | −0.8 | 0.8878 | 250.7 | 6.4 |
| 0.4626 | 617.7 | 4.4 | 0.9230 | 176.3 | 3.9 |
| 0.5057 | 629.8 | 7.7 |  |  |  |
|  |  | Butanoic Acid |  |  |  |
| 0.0890 | 159.9 | −7.1 | 0.6605 | 599.6 | 1.4 |
| 0.1448 | 264.4 | 0.7 | 0.6860 | 575.4 | 0.0 |
| 0.1884 | 338.3 | 3.8 | 0.7141 | 547.2 | 1.8 |
| 0.2668 | 452.6 | 4.1 | 0.7884 | 437.7 | −3.9 |
| 0.3913 | 580.2 | −4.3 | 0.8201 | 383.8 | −3.6 |
| 0.4626 | 629.2 | −0.9 | 0.8728 | 298.4 | 12.7 |
| 0.5230 | 647.4 | 0.8 | 0.9067 | 217.0 | 3.3 |
| 0.5889 | 634.8 | −4.0 | 0.9377 | 129.6 | −15.1 |
| 0.6417 | 615.6 | 3.4 |  |  |  |
|  |  | 2-Methylpropanoic Acid |  |  |  |
| 0.1032 | 276.4 | 8.5 | 0.5013 | 926.8 | 2.5 |
| 0.1870 | 485.8 | 0.8 | 0.5479 | 922.6 | 3.2 |
| 0.2347 | 588.7 | −8.3 | 0.6046 | 896.8 | 8.9 |
| 0.2938 | 720.7 | 3.3 | 0.6531 | 840.1 | 0.6 |
| 0.3508 | 801.3 | −8.7 | 0.6827 | 790.1 | −10.5 |
| 0.3982 | 860.0 | −7.0 | 0.7273 | 718.9 | −10.3 |
| 0.4417 | 902.2 | −0.5 | 0.8013 | 577.9 | −0.9 |
| 0.4547 | 918.7 | 8.5 | 0.8891 | 364.7 | 11.7 |
| 0.4571 | 916.3 | 5.0 | 0.9158 | 273.5 | −1.1 |
|  |  | Pentanoic Acid |  |  |  |
| 0.1197 | 269.0 | −11.0 | 0.6370 | 837.8 | −3.4 |
| 0.1899 | 418.9 | 0.1 | 0.6655 | 815.9 | −2.4 |
| 0.2311 | 501.9 | 7.2 | 0.7138 | 759.6 | −0.8 |
| 0.2782 | 583.1 | 6.9 | 0.7441 | 725.1 | −13.4 |
| 0.4131 | 765.1 | −3.5 | 0.8076 | 584.8 | 5.2 |
| 0.4825 | 831.9 | −0.6 | 0.8487 | 480.9 | 6.7 |
| 0.5404 | 858.1 | −1.9 | 0.9029 | 303.4 | −12.1 |
| 0.5746 | 862.9 | −0.3 | 0.9603 | 119.2 | −11.9 |
| 0.6211 | 845.1 | −5.3 |  |  |  |
|  |  | 3-Methylbutanoic Acid |  |  |  |
| 0.0895 | 190.0 | −6.9 | 0.6283 | 866.9 | −0.6 |
| 0.1287 | 270.0 | −3.4 | 0.6731 | 835.8 | −2.3 |
| 0.1972 | 409.1 | 9.1 | 0.7177 | 792.1 | 5.9 |
| 0.2420 | 486.0 | 6.2 | 0.7515 | 721.9 | −9.5 |
| 0.3371 | 632.1 | −7.2 | 0.7835 | 672.7 | 4.9 |
| 0.4026 | 730.3 | −5.3 | 0.8207 | 571.1 | −8.3 |
| 0.4532 | 799.6 | 2.4 | 0.8529 | 500.9 | 9.3 |
| 0.5200 | 857.0 | 2.7 | 0.8744 | 435.9 | 8.1 |
| 0.5902 | 876.9 | 1.2 | 0.9379 | 206.0 | −13.4 |

Both solvents were dried with 4 Å molecular sieves and degassed before measurements were undertaken.

The liquids were kept in a drybox before use.

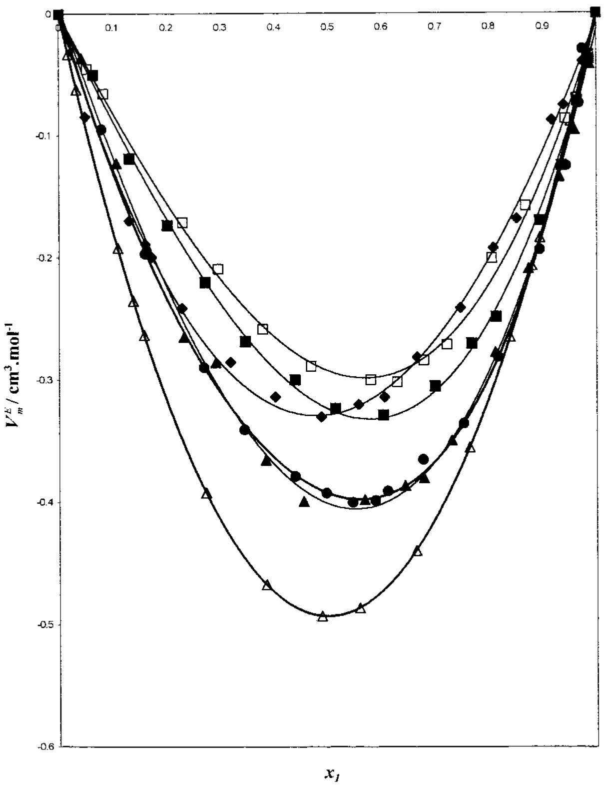

**Figure 2.** Excess molar volumes for the systems [acetonitrile (1) + a carboxylic acid (2)] at 298.15 K, as a function of mole fraction $x_1$: (△) propanoic acid; (▲) butanoic acid; (●) 3-methylbutanoic acid; (◆) acetic acid; (■) pentanoic acid; (□) 2-methylpropanoic acid.

**Table 3. Coefficients $A_r$ and Standard Deviations $\sigma$ from Eq 1 for the Excess Molar Enthalpies of the Systems [acetonitrile (1) + a carboxylic acid (2)] at 298.15 K**

| component | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma(H^E_m)$/ J·mol$^{-1}$ |
|---|---|---|---|---|---|
| acetic acid | 1191.0 | 238.4 | −188.9 | −215.8 | 3.7 |
| propanoic acid | 2486.0 | −233.5 | −307.6 | 63.2 | 5.5 |
| butanoic acid | 2571.0 | −461.5 | −416.2 | 268.7 | 6.1 |
| 2-methylpropanoic acid | 3697.0 | −221.5 | −734.1 | −328.1 | 7.2 |
| pentanoic acid | 3374.0 | −1131.0 | −385.8 | 832.8 | 7.4 |
| 3-methylbutanoic acid | 3362.0 | −1530.0 | −351.6 | 990.1 | 7.2 |

***Procedure.*** An LKB 2107 microcalorimeter was used to determine the molar enthalpies of mixing at 298.15 K. The method has been described previously by Letcher and Scoones (1982). The accuracy was verified using the test mixtures of (hexane + cyclohexane) (McGlashan et al., 1969). Our results agreed with the literature data to within 5 J·mol$^{-1}$.

The densities of the pure liquids and mixtures were measured using an Anton-Paar DMA 602 vibrating-tube densimeter, thermostated at the temperature (298.15 ± 0.005) K. The estimated precision for the excess volume measurements is 0.005 cm$^3$·mol$^{-1}$.

## Results

The measured $H^E_m$ results are given in Figure 1 and Table 2, together with the deviations $\delta H^E_m$, calculated from the smoothing equation

$$\delta H^E_m/(\mathrm{J\cdot mol^{-1}}) = H^E_m/(\mathrm{J\cdot mol^{-1}}) - x(1-x)\sum_{r=0}^{r=k} A_r(1-2x)^r \qquad (1)$$

**Table 4. Correlation of the Excess Molar Enthalpies for the Systems [Acetonitrile (1) + a Carboxylic Acid (2)] by Means of the NRTL and UNIQUAC Equations: Values of Parameters and Measures of Deviations**

| | NRTL[a] | | | UNIQUAC | | |
|---|---|---|---|---|---|---|
| component | $g_{12} - g_{22}$/J·mol$^{-1}$ | $g_{21} - g_{11}$/J·mol$^{-1}$ | $\sigma$/J·mol$^{-1}$ | $\Delta u_{12}$/J·mol$^{-1}$ | $\Delta u_{21}$/J·mol$^{-1}$ | $\sigma$/J·mol$^{-1}$ |
| acetic acid | −146.4 | 1489.0 | 7.485 | −154.5 | 941.1 | 7.440 |
| propanoic acid | 2343.0 | 353.9 | 10.924 | 365.9 | 1009.0 | 11.865 |
| butanoic acid | 2894.0 | −7.8 | 15.897 | 214.2 | 1105.0 | 16.827 |
| 2-methylpropanoic acid | 3055.0 | 1074.0 | 22.768 | 441.9 | 1627.0 | 24.885 |
| pentanoic acid | 4576.0 | −255.2 | 22.018 | 462.2 | 1201.0 | 25.550 |
| 3-methylbutanoic acid | 5419.0 | −663.6 | 24.433 | 674.6 | 958.4 | 29.972 |

[a] Calculated with $\alpha_{12} = 0.2$.

**Table 5. Excess Molar Volumes $V_m^E$ for the Systems [Acetonitrile (1) + a Carboxylic Acid (2)] and the Deviations $\delta V_m^E$, Calculated from Eq 1 and the Parameters of Table 6 at the Experimental Temperature 298.15 K, as a Function of Mole Fraction $x_1$**

| $x_1$ | $V_m^E$/ cm$^3$·mol$^{-1}$ | $10^3\delta V_m^E$/ cm$^3$·mol$^{-1}$ | $x_1$ | $V_m^E$/ cm$^3$·mol$^{-1}$ | $10^3\delta V_m^E$/ cm$^3$·mol$^{-1}$ |
|---|---|---|---|---|---|
| | | Acetic Acid | | | |
| 0.0489 | −0.0846 | −11.0 | 0.6051 | −0.3139 | −5.0 |
| 0.1301 | −0.1699 | −3.0 | 0.6656 | −0.2814 | 7.0 |
| 0.1602 | −0.1889 | 4.0 | 0.7464 | −0.2411 | 3.0 |
| 0.1719 | −0.1997 | 3.0 | 0.8071 | −0.1923 | 6.0 |
| 0.2283 | −0.2413 | 2.0 | 0.8509 | −0.1681 | −8.0 |
| 0.3181 | −0.2854 | 3.0 | 0.9166 | −0.0876 | 6.0 |
| 0.4014 | −0.3136 | −0.9 | 0.9382 | −0.0753 | −5.0 |
| 0.4871 | −0.3301 | −6.0 | 0.9733 | −0.0397 | −9.0 |
| 0.5564 | −0.3201 | −7.0 | | | |
| | | Propanoic Acid | | | |
| 0.0172 | −0.0334 | 0.2 | 0.5579 | −0.4864 | 0.3 |
| 0.0326 | −0.0623 | 0.3 | 0.6637 | −0.4395 | 0.2 |
| 0.1092 | −0.1923 | 0.1 | 0.7631 | −0.3551 | −0.4 |
| 0.1383 | −0.2355 | 0.1 | 0.8386 | −0.2648 | −0.5 |
| 0.1583 | −0.2633 | 0.0 | 0.8793 | −0.2067 | −0.2 |
| 0.2732 | −0.3923 | −0.4 | 0.8942 | −0.1838 | 0.0 |
| 0.3845 | −0.4673 | −0.2 | 0.9509 | −0.0887 | 1.0 |
| 0.4874 | −0.4930 | 0.2 | | | |
| | | Butanoic Acid | | | |
| 0.0422 | −0.0365 | 10.0 | 0.6433 | −0.3864 | −0.1 |
| 0.1070 | −0.1229 | −1.0 | 0.6781 | −0.3803 | −7.0 |
| 0.1624 | −0.1901 | −7.0 | 0.7299 | −0.3493 | −2.0 |
| 0.2322 | −0.2649 | −11.0 | 0.8109 | −0.2774 | 8.0 |
| 0.2908 | −0.2856 | −19.0 | 0.8733 | −0.2091 | 7.0 |
| 0.3836 | −0.3654 | −2.0 | 0.9304 | −0.1342 | −0.2 |
| 0.4541 | −0.399 | −3.0 | 0.9590 | −0.0960 | −12.0 |
| 0.5679 | −0.3981 | 3.0 | 0.9870 | −0.0420 | −14.0 |
| | | 2-Methylpropanoic Acid | | | |
| 0.0518 | −0.0456 | −6.0 | 0.6781 | −0.2839 | −0.7 |
| 0.0829 | −0.0658 | −1.0 | 0.7210 | −0.2712 | 5.0 |
| 0.2300 | −0.1712 | 2.0 | 0.8045 | −0.2008 | 16.0 |
| 0.2959 | −0.2096 | 5.0 | 0.8677 | −0.1578 | 5.0 |
| 0.3780 | −0.2586 | −2.0 | 0.9415 | −0.0868 | −6.0 |
| 0.4686 | −0.2889 | −0.6 | 0.9623 | −0.0699 | −16.0 |
| 0.5794 | −0.2999 | 0.5 | 0.9850 | −0.0346 | −12.0 |
| 0.6290 | −0.3019 | −7.0 | | | |
| | | Pentanoic Acid | | | |
| 0.0631 | −0.0502 | 3.0 | 0.6986 | −0.3049 | −0.4 |
| 0.1299 | −0.1189 | −6.0 | 0.7661 | −0.2699 | 7.0 |
| 0.2006 | −0.1734 | −0.6 | 0.8120 | −0.2483 | 0.2 |
| 0.2711 | −0.2201 | 4.0 | 0.8935 | −0.1696 | 3.0 |
| 0.3451 | −0.2683 | −0.8 | 0.9340 | −0.1247 | −6.0 |
| 0.4374 | −0.2997 | −4.0 | 0.9634 | −0.0720 | −1.0 |
| 0.5132 | −0.3231 | −3.0 | 0.9851 | −0.0375 | −7.0 |
| 0.6021 | −0.3286 | −6.0 | | | |
| | | 3-Methylbutanoic Acid | | | |
| 0.0791 | −0.0950 | 5.0 | 0.6105 | −0.3910 | 0.1 |
| 0.1601 | −0.1970 | −5.0 | 0.6766 | −0.3653 | 7.0 |
| 0.2694 | −0.2899 | 1.0 | 0.7520 | −0.3356 | −2.0 |
| 0.3441 | −0.3406 | 0.3 | 0.8162 | −0.2810 | 1.0 |
| 0.4389 | −0.3789 | 2.0 | 0.8937 | −0.1936 | −2.0 |
| 0.4964 | −0.3925 | 1.0 | 0.9434 | −0.1253 | −11.0 |
| 0.5456 | −0.4002 | −3.0 | 0.9672 | −0.0740 | −5.0 |
| 0.5879 | −0.3988 | −4.0 | 0.9737 | −0.0298 | 27.0 |

**Table 6. Coefficients $A_r$ and Standard Deviations $\sigma$ from Eq 1 for the Excess Molar Volumes of the Systems [Acetonitrile (1) + a Carboxylic Acid (2)] at 298.15 K**

| component | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $10^2$·$\sigma(V_m^E)$/ cm$^3$·mol$^{-1}$ |
|---|---|---|---|---|---|
| acetic acid | −1.295 | −0.017 | −0.122 | −0.238 | 0.6 |
| propanoic acid | −1.974 | −0.002 | 0.022 | −0.032 | 0.1 |
| butanoic acid | −1.597 | 0.259 | −0.058 | 0.322 | 0.9 |
| 2-methylpropanoic acid | −1.179 | 0.343 | 0.042 | 0.031 | 0.8 |
| pentanoic acid | −1.272 | 0.311 | −0.192 | 0.359 | 0.5 |
| 3-methylbutanoic acid | −1.576 | 0.252 | −0.208 | 0.240 | 0.9 |

where $x$ is the mole fraction of acetonitrile and $r = 0, 1, 2,$ or 3. The values of the parameters $A_r$ are given in Table 3, together with the standard deviation $\sigma$.

$$\sigma = [\sum(H^E_{m(expt)} - H^E_{m(calc)})^2/N - a]^{1/2} \tag{2}$$

where $N$ is the number of experimental points and $a$ is the number of fitting coefficients.

The measured $V_m^E$ results are given in Figure 2 and Table 5, together with the deviations $\delta V_m^E$, calculated from the smoothing eq 1 of corresponding form. The values of the parameters $A_r$ are given in Table 6, together with the standard deviation $\sigma$, calculated using eq 2 of corresponding form.

Two thermodynamic models, namely the nonrandom two-liquid equation NRTL (Renon and Prausnitz, 1967) and the universal quasichemical equation UNIQUAC (Abrams and Prausnitz,1975), were both fitted to the excess molar enthalpy data. The NRTL interaction parameters $g_{12} - g_{22}$, and $g_{21} - g_{11}$ are given in Table 4 together with the standard deviations. The UNIQUAC interaction parameters $\Delta u_{12}$ and $\Delta u_{21}$ are also given in Table 4 together with the corresponding standard deviations. The standard deviation $\sigma$ for the NRTL and the UNIQUAC models is defined as

$$\sigma = [\sum(H^E_{m(expt)} - H^E_{m(calc)})^2/N]^{1/2} \tag{3}$$

where $N$ is the number of experimental points.

## Discussion

The $H_m^E$ values for the mixtures under investigation are positive over the whole composition range, and the magnitude decreases in the order 2-methylpropanoic acid > 3-methylbutanoic acid ∼ pentanoic acid > butanoic acid ∼ propanoic acid > acetic acid. Acetonitrile is a typical aprotic, dipolar, simple organic liquid with a carbon−nitrogen triple bond and an unshared electron pair. X-ray analysis on pure acetonitrile has revealed that the linear acetonitrile dipoles are arranged in antiparallel positions and that definite short-range ordering between molecules is due to the dipole−dipole interaction (Brown and Smith, 1962). The carboxylic acids in pure form tend to exist mainly as dimers. The overall magnitude of $H_m^E[x_1CH_3CN$

+ (1 − $x_1$)RCOOH] is therefore most probably due to the breakdown of the acetonitrile self-association (a positive enthalpy), the breakdown of the carboxylic acid (dimers) self-association (a positive enthalpy), and the negative effect of the (acetonitrile−carboxylic acid) association. The results of this work indicate in general that the longer the alkyl group of the carboxylic acid, the weaker is the interaction with acetonitrile, and it appears as though the long alkyl groups shield the carbonyl oxygen atom of the carboxylic acid from interaction. The results have been interpreted by assuming n−$\pi$ interactions to occur between the lone-pair electrons of the oxygen atom and the $\pi$ electrons of acetonitrile. The results also indicate that in the case of the branched carboxylic acids, viz., 2-methylpropanoic acid and 3-methylbutanoic acid, the increase in steric crowding due to the methyl groups as well as increasing dimerization constants, leads to a increase in the excess enthalpy.

The excess molar volumes for all six systems are given in Table 5. The results are negative for all six systems over the entire composition range at 298.15 K. The excess molar volumes are most negative in the case of propanoic acid ($< -0.5$ cm$^3$·mol$^{-1}$), and the magnitude decreases in the following order: propanoic acid > butanoic acid ∼ 3-methylbutanoic acid > acetic acid ∼ pentanoic acid > 2-methylpropanoic acid.

It is difficult to separate the volume change contributions due to packing effects from intermolecular effects. If the packing effects were insignificant, then one might expect the largest $V_m^E$ for the system (acetonitrile + acetic acid). This is not true, and thus one must assume that the packing effects are also important. It is also found that the position of the minima for $V_m^E$ (acetonitrile + acetic acid) shifts slowly to the acetonitrile-rich region of the mole fraction scale as the methylation of acetic acid increases. This could possibly be explained by the increase in both the dimerization constants as well as the increasing steric hindrance caused by additional methyl groups. This is further supported by the findings of Cibulka et al., (1984) who have shown that, for binary systems containing alkanol and acetonitrile, $V^E$ increases in the order: $V^E$ (acetonitrile + normal alkanol) < $V^E$ (acetonitrile + branched alkanol) < $V^E$ (acetonitrile + secondary alkanol).

The $V_m^E$ results obtained for the systems (acetonitrile + acetic acid or propanoic acid or 2-methylpropanoic acid) have previously been reported by Lark and Banipal (1984). In all cases our results are within 0.05 cm$^3$·mol$^{-1}$ of their values.

As can be observed from Table 4, both the NRTL and UNIQUAC models fitted the excess molar enthalpy data equally well.

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