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### Excess Volumes and Excess Viscosities of Binary Mixtures of Cyclohexane an Isomer of Butanol at Several Temperatures

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## EXCESS VOLUMES AND EXCESS VISCOSITIES OF BINARY MIXTURES OF CYCLOHEXANE + AN ISOMER OF BUTANOL AT SEVERAL TEMPERATURES

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From density and viscosity measurements of binary mixtures of cyclohexane with an isomer of butanol at several temperatures, excess volumes  $V^E$ , excess viscosities  $\eta^E$  and excess energies of activation for viscous flow  $G^{*E}$  have been determined at different temperatures. The results have been correlated by a Redlich-Kister type equation and discussed in terms of molecular interactions. While  $V^E$  values are positive over the whole composition range for all mixtures at all temperatures, both  $\eta^E$  and  $G^{*E}$  are negative.

KEY WORDS: Binary mixtures; cyclohexane; excess volumes; excess viscosities; excess energies of activation for viscous flow; isomeric butanols; several temperatures.

### INTRODUCTION

Continuing with our research program of excess thermodynamic and excess flow properties in binary mixtures of an alkane or haloalkane with associated organic liquids (picolines or the alcoholic isomers of butanol)<sup>1–5</sup>, now we present the results obtained for  $V^E$ ,  $\eta^E$  and  $G^{*E}$  for the mixtures of cyclohexane with isomeric butanol at the temperatures 293.15, 303.15 and 313.15 K, except for the mixtures with 2-methyl-2-propanol, that have been done at 303.15 and 313.15 K. One reference was found<sup>6</sup> but it was not available in order to compare our results.

### EXPERIMENTAL

All pure components used were provided by Aldrich, and their purities were: cyclohexane (better than 99.9 mol%), 1-butanol (better than 99.8 mol%), 2-methyl-1-propanol and 2-methyl-2-propanol (better than 99.5 mol %) and 2-butanol (better than 99 mol%). The purity of the chemicals was checked by GLC using a semicapillary methyl silicone column (o.d. 530  $\mu\text{m}$ ) and a flame ionization detector. The analysis

showed that the major peak area exceeds 99.8%, so no further purification was considered necessary. Each isomeric butanol was stored over activated molecular sieve type 0.3 nm from Merck.

Table 1 shows the experimental values of density and viscosity for the pure components at  $T = 303.15$  K compared with published values<sup>7</sup>.

Densities were measured with an Anton Paar DMA-58 vibrating tube densimeter, and viscosities were determined using an Ubbelohde viscosimeter with a Schott-Geräte automatic measuring unit model AVS-440. Details of the procedure for the measurement of density and viscosity can be found in previous articles<sup>1,5</sup>.

## RESULTS AND DISCUSSION

The excess functions were calculated from our measurements according to the following equations:

$$V^E = x_1 M_1(\rho^{-1} - \rho_1^{-1}) + x_2 M_2(\rho^{-1} - \rho_2^{-1}) \quad (1)$$

$$\eta^E = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (2)$$

$$G^{*E} = RT[\ln \eta V - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \quad (3)$$

where  $\rho, \rho_1$  and  $\rho_2$  are the densities ( $\text{g} \cdot \text{cm}^{-3}$ ) of the mixtures and of the pure components respectively;  $\eta, \eta_1$  and  $\eta_2$  are the absolute viscosities ( $\text{cP}$ ) of the mixtures and of the pure components;  $V, V_1$  and  $V_2$  are the molar volumes ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) of the mixture and of the pure components, and  $x_i$  is the mole fraction of component  $i$  in the mixture.

The excess functions for the mixtures at their correspondent temperature are gathered in Tables 2–4. They are graphically presented in Figures 1–9.

The values of  $V^E, \eta^E$  and  $G^{*E}$  were fitted at each temperature to a Redlich-Kister type equation by the least squares method:

$$Y^E = x_1(1 - x_1) \sum a_i(2x_1 - 1)^i \quad (4)$$

where  $a_i$  are adjustable parameters and  $x_1$  is the mole fraction of cyclohexane. The values of the parameters  $a_i$  together with the standard deviations  $\sigma(Y^E)$  are given in Table 5.

**Table 1** Densities  $\rho$ , and viscosities  $\eta$ , of pure compounds at  $T = 303.15$  K and comparison with literature data<sup>7</sup>.

| Component           | $\rho/\text{gcm}^{-3}$ |             | $\eta/\text{cP}$  |             |
|---------------------|------------------------|-------------|-------------------|-------------|
|                     | <i>this paper</i>      | <i>lit.</i> | <i>this paper</i> | <i>lit.</i> |
| Cyclohexane         | 0.76900                | 0.76918     | 0.8196            | 0.8240      |
| 1-Butanol           | 0.80193                | 0.8022      | 2.2537            | 2.2630      |
| 2-Butanol           | 0.79828                | 0.7984      | 2.5244            | 2.4989      |
| 2-Methyl-1-propanol | 0.79390                | 0.7938      | 2.8871            | 2.8466      |
| 2-Methyl-2-propanol | 0.77561                | 0.7757      | 3.3374            | 3.3900      |

**Table 2** Excess volumes  $V^E$  of binary mixtures cyclohexane (1) + isomeric butanol (2) at indicated temperature.

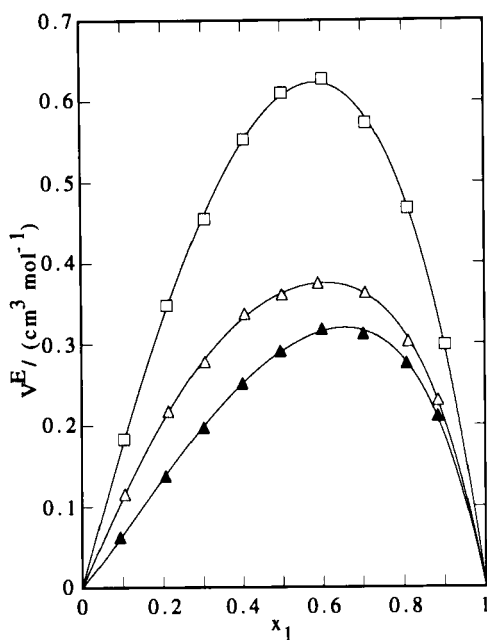
| $x_1$   | $V^E/cm^3 mol^{-1}$ | $x_1$  | $V^E/cm^3 mol^{-1}$ | $x_1$  | $V^E/cm^3 mol^{-1}$ |
|---|---------------------|--------|---------------------|--------|---------------------|
| Cyclohexane + 1-butanol at 293.15 K           |                     |        |                     |        |                     |
| 0.1042  | 0.1157              | 0.4057 | 0.3375              | 0.7072 | 0.3632              |
| 0.2143  | 0.2177              | 0.4997 | 0.3611              | 0.8123 | 0.3031              |
| 0.3048  | 0.2780              | 0.5892 | 0.3753              | 0.8853 | 0.2305              |
| Cyclohexane + 2-butanol at 293.15 K           |                     |        |                     |        |                     |
| 0.1032  | 0.1832              | 0.4054 | 0.5532              | 0.7100 | 0.5733              |
| 0.2115  | 0.3480              | 0.5009 | 0.6102              | 0.8120 | 0.4679              |
| 0.3061  | 0.4550              | 0.6029 | 0.6275              | 0.9032 | 0.2986              |
| Cyclohexane + 2-methyl-1-propanol at 293.15 K |                     |        |                     |        |                     |
| 0.0923  | 0.0626              | 0.3991 | 0.2513              | 0.7025 | 0.3126              |
| 0.2064  | 0.1378              | 0.4951 | 0.2912              | 0.8077 | 0.2759              |
| 0.3012  | 0.1973              | 0.5987 | 0.3181              | 0.8843 | 0.2110              |
| Cyclohexane + 1-butanol at 303.15 K           |                     |        |                     |        |                     |
| 0.1295  | 0.1175              | 0.4029 | 0.3600              | 0.7082 | 0.3953              |
| 0.2107  | 0.2146              | 0.5006 | 0.3991              | 0.8152 | 0.3417              |
| 0.3059  | 0.3045              | 0.6018 | 0.4139              | 0.8848 | 0.2668              |
| Cyclohexane + 2-butanol at 303.15 K           |                     |        |                     |        |                     |
| 0.1016  | 0.1890              | 0.4068 | 0.5936              | 0.7088 | 0.6380              |
| 0.2157  | 0.3710              | 0.5038 | 0.6495              | 0.8153 | 0.5126              |
| 0.3065  | 0.4871              | 0.6018 | 0.6822              | 0.8915 | 0.3681              |
| Cyclohexane + 2-methyl-1-propanol at 303.15 K |                     |        |                     |        |                     |
| 0.0957  | 0.0759              | 0.3995 | 0.2786              | 0.7038 | 0.3831              |
| 0.2094  | 0.1599              | 0.4945 | 0.3319              | 0.8083 | 0.3325              |
| 0.3037  | 0.2189              | 0.5987 | 0.3771              | 0.8821 | 0.2569              |
| Cyclohexane + 2-methyl-2-propanol at 303.15 K |                     |        |                     |        |                     |
| 0.1101  | 0.2903              | 0.4108 | 0.8172              | 0.7219 | 0.6456              |
| 0.2193  | 0.5716              | 0.5179 | 0.8094              | 0.8209 | 0.5020              |
| 0.3575  | 0.7873              | 0.6156 | 0.7521              | 0.8851 | 0.3900              |
| Cyclohexane + 1-butanol at 313.15 K           |                     |        |                     |        |                     |
| 0.1046  | 0.1144              | 0.4013 | 0.3934              | 0.7072 | 0.4450              |
| 0.2111  | 0.2394              | 0.4992 | 0.4262              | 0.8134 | 0.3827              |
| 0.3026  | 0.3232              | 0.5953 | 0.4481              | 0.9005 | 0.2710              |
| Cyclohexane + 2-butanol at 313.15 K           |                     |        |                     |        |                     |
| 0.1069  | 0.2151              | 0.4081 | 0.6786              | 0.7100 | 0.7158              |
| 0.2149  | 0.4090              | 0.5036 | 0.7501              | 0.8156 | 0.5780              |
| 0.3085  | 0.5632              | 0.6037 | 0.7667              | 0.9059 | 0.3560              |
| Cyclohexane + 2-methyl-1-propanol at 313.15 K |                     |        |                     |        |                     |
| 0.1076  | 0.1088              | 0.4073 | 0.3455              | 0.7120 | 0.4390              |
| 0.2170  | 0.2124              | 0.5057 | 0.4123              | 0.8010 | 0.3824              |
| 0.3101  | 0.2815              | 0.6095 | 0.4428              | 0.9075 | 0.2285              |
| Cyclohexane + 2-methyl-2-propanol at 313.15 K |                     |        |                     |        |                     |
| 0.1087  | 0.3695              | 0.4148 | 0.8459              | 0.7151 | 0.7092              |
| 0.2205  | 0.6351              | 0.5118 | 0.8532              | 0.8252 | 0.5601              |
| 0.3164  | 0.7780              | 0.6088 | 0.8102              | 0.8922 | 0.4276              |

**Table 3** Excess viscosities  $\eta^E$  of binary mixtures cyclohexane (1)+isomeric butanol (2) at indicated temperature.

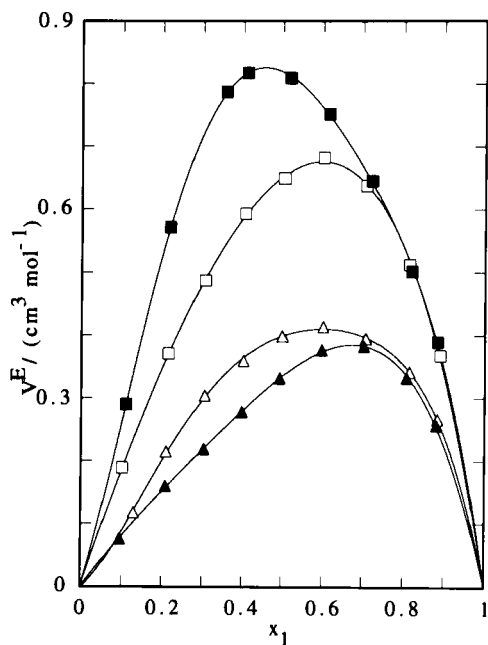
| $x_1$   | $\eta^E/cP$ | $x_1$  | $\eta^E/cP$ | $x_1$  | $\eta^E/cP$ |
|---|-------------|--------|-------------|--------|-------------|
| Cyclohexane + 1-butanol at 293.15 K           |             |        |             |        |             |
| 0.0994  | -0.1858     | 0.4031 | -0.4768     | 0.6921 | -0.4450     |
| 0.1960  | -0.3023     | 0.5091 | -0.5060     | 0.8105 | -0.3211     |
| 0.3067  | -0.4223     | 0.6207 | -0.4861     | 0.9035 | -0.1851     |
| Cyclohexane + 2-butanol at 293.15 K           |             |        |             |        |             |
| 0.0995  | -0.6350     | 0.3994 | -1.1258     | 0.6919 | -0.7762     |
| 0.2033  | -0.9648     | 0.5078 | -1.0588     | 0.8011 | -0.5339     |
| 0.2962  | -1.0983     | 0.6001 | -0.9421     | 0.8846 | -0.3280     |
| Cyclohexane + 2-methyl-1-propanol at 293.15 K |             |        |             |        |             |
| 0.0991  | -0.3940     | 0.4018 | -0.9151     | 0.7002 | -0.7190     |
| 0.1996  | -0.6708     | 0.4638 | -0.9207     | 0.8011 | -0.5194     |
| 0.2996  | -0.8388     | 0.6002 | -0.8544     | 0.8964 | -0.2920     |
| Cyclohexane + 1-butanol at 303.15 K           |             |        |             |        |             |
| 0.0994  | -0.1430     | 0.4031 | -0.3689     | 0.6921 | -0.3326     |
| 0.1960  | -0.2442     | 0.5091 | -0.3882     | 0.8105 | -0.2388     |
| 0.3067  | -0.3258     | 0.6207 | -0.3671     | 0.9035 | -0.1391     |
| Cyclohexane + 2-butanol at 303.15 K           |             |        |             |        |             |
| 0.0995  | -0.3869     | 0.3994 | -0.7100     | 0.6919 | -0.4942     |
| 0.2033  | -0.6003     | 0.5078 | -0.6658     | 0.8011 | -0.3450     |
| 0.2962  | -0.6871     | 0.6001 | -0.5971     | 0.8846 | -0.2152     |
| Cyclohexane + 2-methyl-1-propanol at 303.15 K |             |        |             |        |             |
| 0.0991  | -0.2565     | 0.4018 | -0.6237     | 0.7002 | -0.4889     |
| 0.1996  | -0.4486     | 0.4638 | -0.6290     | 0.8011 | -0.3536     |
| 0.2996  | -0.5683     | 0.6002 | -0.5811     | 0.8964 | -0.2003     |
| Cyclohexane + 2-methyl-2-propanol at 303.15 K |             |        |             |        |             |
| 0.1006  | -0.8090     | 0.4040 | -1.1533     | 0.6962 | -0.6871     |
| 0.1986  | -1.1195     | 0.5005 | -1.0362     | 0.8001 | -0.4723     |
| 0.3009  | -1.2054     | 0.5959 | -0.8788     | 0.9020 | -0.2477     |
| Cyclohexane + 1-butanol at 313.15 K           |             |        |             |        |             |
| 0.0994  | -0.1085     | 0.4031 | -0.2800     | 0.6921 | -0.2495     |
| 0.1960  | -0.1852     | 0.5091 | -0.2939     | 0.8105 | -0.1785     |
| 0.3067  | -0.2454     | 0.6207 | -0.2765     | 0.9035 | -0.1065     |
| Cyclohexane + 2-butanol at 313.15 K           |             |        |             |        |             |
| 0.0995  | -0.2403     | 0.3994 | -0.4546     | 0.6919 | -0.3226     |
| 0.2033  | -0.3788     | 0.5078 | -0.4320     | 0.8011 | -0.2280     |
| 0.2962  | -0.4392     | 0.6001 | -0.3869     | 0.8846 | -0.1459     |
| Cyclohexane + 2-methyl-1-propanol at 313.15 K |             |        |             |        |             |
| 0.0991  | -0.1775     | 0.4018 | -0.4378     | 0.7002 | -0.3390     |
| 0.1996  | -0.3132     | 0.4638 | -0.4384     | 0.8011 | -0.2461     |
| 0.2996  | -0.4002     | 0.6002 | -0.4053     | 0.8964 | -0.1415     |
| Cyclohexane + 2-methyl-2-propanol at 313.15 K |             |        |             |        |             |
| 0.1006  | -0.3910     | 0.4040 | -0.5951     | 0.6962 | -0.3736     |
| 0.1986  | -0.5552     | 0.5005 | -0.5422     | 0.8001 | -0.2629     |
| 0.3009  | -0.6095     | 0.5959 | -0.4672     | 0.9020 | -0.1426     |

**Table 4** Excess energies of activation for viscous flow  $G^{*E}$  of binary mixtures cyclohexane (1) + isomeric butanol (2) at indicated temperature.

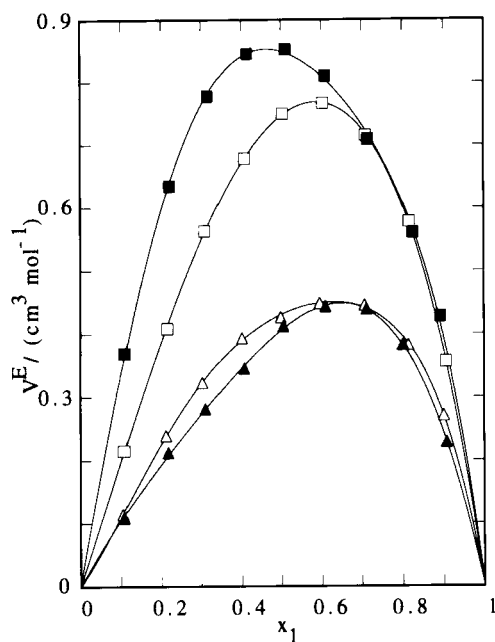
| $x_1$   | $G^{*E}/J\ mol^{-1}$ | $x_1$  | $G^{*E}/J\ mol^{-1}$ | $x_1$  | $G^{*E}/J\ mol^{-1}$ |
|---|----------------------|--------|----------------------|--------|----------------------|
| Cyclohexane + 1-butanol at 293.15 K           |                      |        |                      |        |                      |
| 0.0994  | -65.9                | 0.4031 | -279.6               | 0.6921 | -446.7               |
| 0.1960  | -112.9               | 0.5091 | -367.8               | 0.8105 | -376.1               |
| 0.3067  | -208.0               | 0.6207 | -433.5               | 0.9035 | -243.0               |
| Cyclohexane + 2-butanol at 293.15 K           |                      |        |                      |        |                      |
| 0.0995  | -355.0               | 0.3994 | -908.6               | 0.6919 | -832.0               |
| 0.2033  | -615.8               | 0.5078 | -962.1               | 0.8011 | -613.5               |
| 0.2962  | -786.2               | 0.6001 | -939.0               | 0.8846 | -400.4               |
| Cyclohexane + 2-methyl-1-propanol at 293.15 K |                      |        |                      |        |                      |
| 0.0991  | -117.6               | 0.4018 | -454.1               | 0.7002 | -584.9               |
| 0.1996  | -237.7               | 0.4638 | -505.6               | 0.8011 | -473.3               |
| 0.2996  | -351.6               | 0.6002 | -600.1               | 0.8964 | -295.3               |
| Cyclohexane + 1-butanol at 303.15 K           |                      |        |                      |        |                      |
| 0.0994  | -82.4                | 0.4031 | -328.1               | 0.6921 | -453.2               |
| 0.1960  | -158.2               | 0.5091 | -411.0               | 0.8105 | -370.1               |
| 0.3067  | -248.7               | 0.6207 | -456.3               | 0.9035 | -239.5               |
| Cyclohexane + 2-butanol at 303.15 K           |                      |        |                      |        |                      |
| 0.0995  | -337.5               | 0.3994 | -862.6               | 0.6919 | -757.0               |
| 0.2033  | -593.6               | 0.5078 | -887.3               | 0.8011 | -564.1               |
| 0.2962  | -751.4               | 0.6001 | -861.4               | 0.8846 | -372.4               |
| Cyclohexane + 2-methyl-1-propanol at 303.15 K |                      |        |                      |        |                      |
| 0.0991  | -119.3               | 0.4018 | -476.1               | 0.7002 | -562.0               |
| 0.1996  | -250.3               | 0.4638 | -524.7               | 0.8011 | -446.9               |
| 0.2996  | -372.5               | 0.6002 | -591.7               | 0.8964 | -278.3               |
| Cyclohexane + 2-methyl-2-propanol at 303.15 K |                      |        |                      |        |                      |
| 0.1006  | -600.7               | 0.4040 | -1192.9              | 0.6962 | -825.6               |
| 0.1986  | -953.8               | 0.5005 | -1139.0              | 0.8001 | -597.5               |
| 0.3009  | -1148.0              | 0.5959 | -1012.1              | 0.9020 | -340.0               |
| Cyclohexane + 1-butanol at 313.15 K           |                      |        |                      |        |                      |
| 0.0994  | -91.1                | 0.4031 | -347.6               | 0.6921 | -445.3               |
| 0.1960  | -173.2               | 0.5091 | -424.2               | 0.8105 | -355.3               |
| 0.3067  | -264.0               | 0.6207 | -457.1               | 0.9035 | -220.7               |
| Cyclohexane + 2-butanol at 313.15 K           |                      |        |                      |        |                      |
| 0.0995  | -312.3               | 0.3994 | -787.8               | 0.6919 | -678.5               |
| 0.2033  | -550.5               | 0.5078 | -813.0               | 0.8011 | -507.7               |
| 0.2962  | -698.0               | 0.6001 | -773.5               | 0.8846 | -344.1               |
| Cyclohexane + 2-methyl-1-propanol at 313.15 K |                      |        |                      |        |                      |
| 0.0991  | -128.1               | 0.4018 | -492.3               | 0.7002 | -531.5               |
| 0.1996  | -266.9               | 0.4638 | -528.0               | 0.8011 | -418.8               |
| 0.2996  | -395.8               | 0.6002 | -577.7               | 0.8964 | -264.2               |
| Cyclohexane + 2-methyl-2-propanol at 313.15 K |                      |        |                      |        |                      |
| 0.1006  | -473.5               | 0.4040 | -941.0               | 0.6962 | -681.5               |
| 0.1986  | -749.4               | 0.5005 | -902.8               | 0.8001 | -506.0               |
| 0.3009  | -898.5               | 0.5959 | -812.9               | 0.9020 | -296.6               |



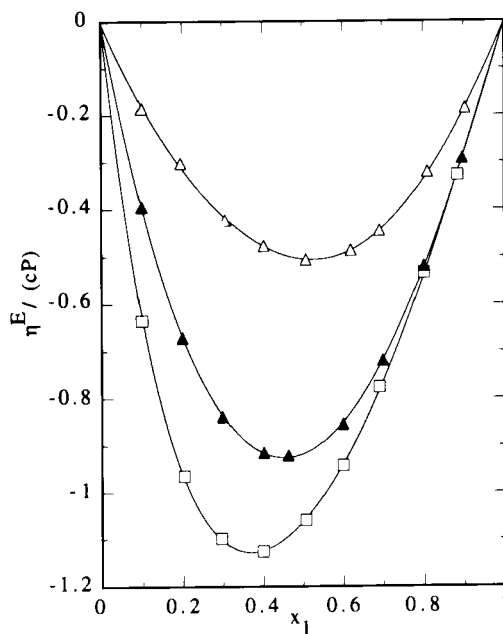
**Figure 1** Excess volumes,  $V^E$ , of cyclohexane (1) + a butanol (2) at 293.15 K as a function of mole fraction  $x_1$ : 1-butanol ( $\Delta$ ); 2-butanol ( $\square$ ); 2-methyl-1-propanol ( $\blacktriangle$ ).



**Figure 2** Excess volumes,  $V^E$ , of cyclohexane (1) + a butanol (2) at 303.15 K as a function of mole fraction  $x_1$ : 1-butanol ( $\Delta$ ); 2-butanol ( $\square$ ); 2-methyl-1-propanol ( $\blacktriangle$ ); 2-methyl-2-propanol ( $\blacksquare$ ).

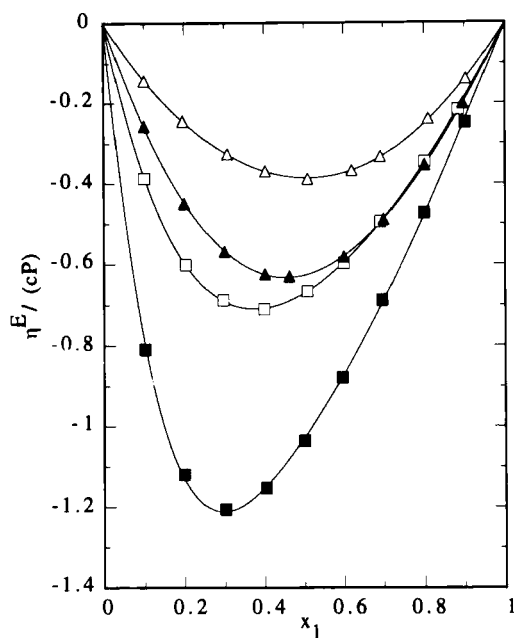


**Figure 3** Excess volumes,  $V^E$ , of cyclohexane (1) + a butanol (2) at 313.15 K as a function of mole fraction  $x_1$ : 1-butanol ( $\Delta$ ); 2-butanol ( $\square$ ); 2-methyl-1-propanol ( $\blacktriangle$ ); 2-methyl-2-propanol ( $\blacksquare$ ).

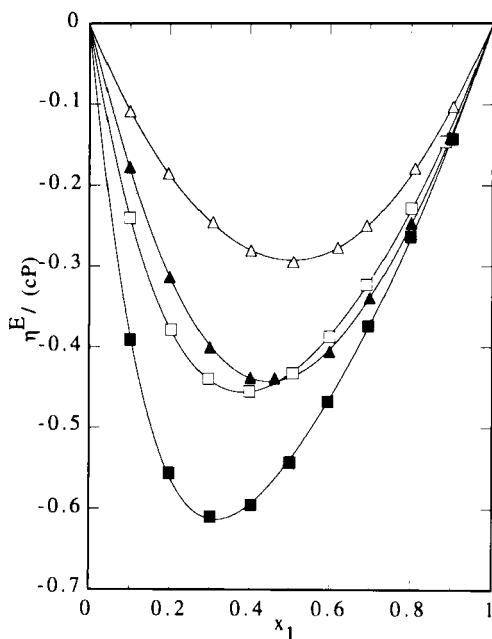


**Figure 4** Excess viscosities,  $\eta^E$ , of cyclohexane (1) + a butanol (2) at 298.15 K as a function of mole fraction  $x_1$ : 1-butanol ( $\Delta$ ); 2-butanol ( $\square$ ); 2-methyl-1-propanol ( $\blacktriangle$ ).

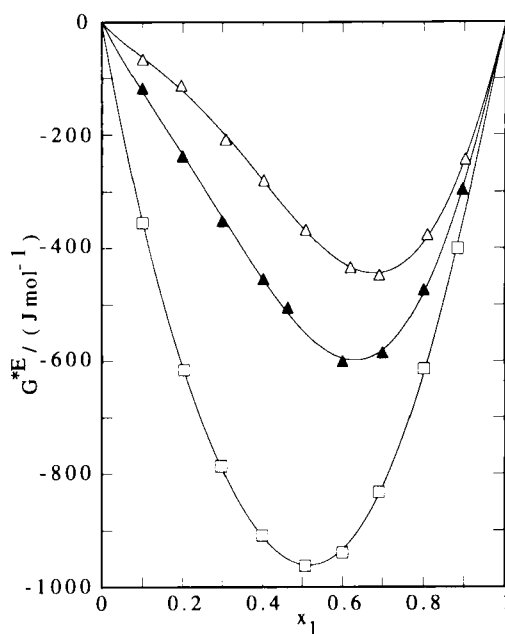




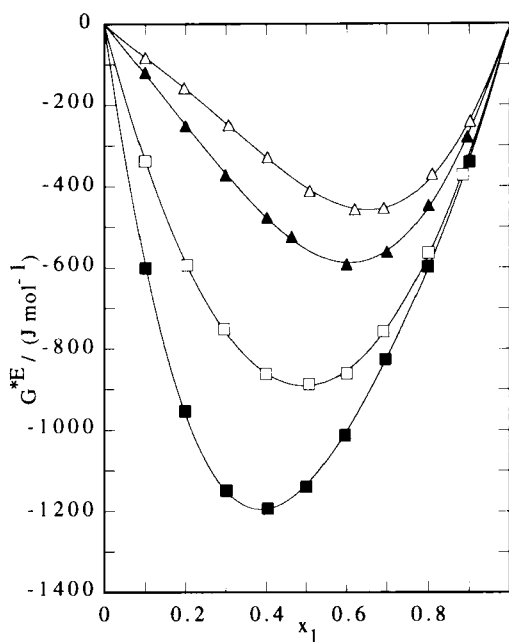
**Figure 5** Excess viscosities,  $\eta^E$ , of cyclohexane (1) + a butanol (2) at 303.15 K as a function of mole fraction  $x_1$ : 1-butanol ( $\Delta$ ); 2-butanol ( $\square$ ); 2-methyl-1-propanol ( $\blacktriangle$ ); 2-methyl-2-propanol ( $\blacksquare$ ).



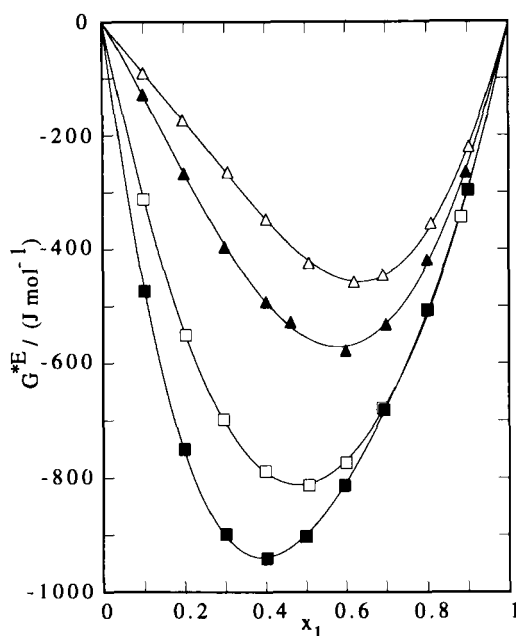
**Figure 6** Excess viscosities,  $\eta^E$ , of cyclohexane (1) + a butanol (2) at 313.15 K as a function of mole fraction  $x_1$ : 1-butanol ( $\Delta$ ); 2-butanol ( $\square$ ); 2-methyl-1-propanol ( $\blacktriangle$ ); 2-methyl-2-propanol ( $\blacksquare$ ).



**Figure 7** Excess energies of activation for viscous flow,  $G^{*E}$ , of cyclohexane(1) + a butanol(2) at 293.15 K as a function of mole fraction  $x_1$ : 1-butanol ( $\Delta$ ); 2-butanol ( $\square$ ); 2-methyl-1-propanol ( $\blacktriangle$ ).



**Figure 8** Excess energies of activation for viscous flow,  $G^{*E}$ , of cyclohexane(1) + a butanol(2) at 303.15 K as a function of mole fraction  $x_1$ : 1-butanol ( $\Delta$ ); 2-butanol ( $\square$ ); 2-methyl-1-propanol ( $\blacktriangle$ ); 2-methyl-2-propanol ( $\blacktriangle$ ).



**Figure 9** Excess energies of activation for viscous flow,  $G^{*E}$ , of cyclohexane(1) + a butanol(2) at 313.15 K as a function of mole fraction  $x_1$ : 1-butanol ( $\Delta$ ); 2-butanol ( $\square$ ); 2-methyl-1-propanol ( $\blacktriangle$ ); 2-methyl-2-propanol ( $\blacksquare$ ).

The excess volumes are positive over the whole composition range and increase when temperature rises.  $V^E$  increases following the sequence:

$$2\text{-methyl-1-propanol} < 1\text{-butanol} < 2\text{-butanol} < 2\text{-methyl-2-propanol}.$$

The alkanols are self-associated liquids by hydrogen bonding<sup>8</sup>. The addition of a non polar liquid, like cyclohexane, breaks the molecular order and leads to positive values of  $V^E$ . This breaking increases when  $T$  increases. Maximum values shift towards higher concentrations of cyclohexane reversing the above mentioned sequence.

The excess viscosities  $\eta^E$  and excess energies of activation for viscous flow  $G^{*E}$  are negative over the whole composition range. When  $T$  grows up, both  $\eta^E$  and  $G^{*E}$  increases for all mixtures, except for those with 1-butanol, in which  $G^{*E}$  becomes slightly more negative. Minimum  $\eta^E$  and  $G^{*E}$  values shift towards lower concentrations of cyclohexane following the sequence:

$$1\text{-butanol} < 2\text{-methyl-1-propanol} < 2\text{-butanol} < 2\text{-methyl-2-propanol}.$$

When  $T$  rises, the position of minimum values does not change, except for mixtures containing 1-butanol, where at 293.15 K the minimum appears for a molar fraction bigger than for the other temperatures. According to Meyer *et al.*<sup>9</sup> or Nigam *et al.*<sup>10</sup>, negative  $G^{*E}$  values denote a characteristic behavior of liquid systems where dispersion forces, like the breaking of the association of butanols, are prevalent. In the same way, negative values of  $\eta^E$  and  $G^{*E}$  correspond, in accordance with Fort and Moore<sup>11</sup>, with

**Table 5** Coefficients  $a_i$  of equation (4) and standard deviations determined by the method of least squares.

| Function                                      | $a_0$   | $a_1$   | $a_2$   | $a_3$   | $\sigma$ |
|---|---------|---------|---------|---------|----------|
| Cyclohexane + 1-butanol at 293.15 K           |         |         |         |         |          |
| $V^E/\text{cm}^3 \text{ mol}^{-1}$            | 1.4522  | 0.4529  | 0.4882  | 0.3395  | 0.0033   |
| $\eta^E/\text{cP}$                            | -2.0187 | -0.1917 | -0.0525 | 0.2170  | 0.0052   |
| $G^{*E}/\text{J mol}^{-1}$                    | -1451.0 | -1533.9 | -424.6  | 388.6   | 5.7      |
| Cyclohexane + 2-butanol at 293.15 K           |         |         |         |         |          |
| $V^E/\text{cm}^3 \text{ mol}^{-1}$            | 2.4259  | 0.7617  | 0.3513  | 0.1629  | 0.0060   |
| $\eta^E/\text{cP}$                            | -4.2493 | 1.8792  | -1.2551 | 0.8778  | 0.0063   |
| $G^{*E}/\text{J mol}^{-1}$                    | -3839.2 | -255.5  | -55.2   | 501.0   | 6.4      |
| Cyclohexane + 2-methyl-1-propanol at 293.15 K |         |         |         |         |          |
| $V^E/\text{cm}^3 \text{ mol}^{-1}$            | 1.1658  | 0.6568  | 0.3800  | 0.3038  | 0.0030   |
| $\eta^E/\text{cP}$                            | -3.6729 | 0.6648  | -0.1714 | 0.2479  | 0.0039   |
| $G^{*E}/\text{J mol}^{-1}$                    | -2179.1 | -1490.0 | -155.4  | 581.8   | 7.4      |
| Cyclohexane + 1-butanol at 303.15 K           |         |         |         |         |          |
| $V^E/\text{cm}^3 \text{ mol}^{-1}$            | 1.5971  | 0.4480  | 0.3723  | 0.9843  | 0.0036   |
| $\eta^E/\text{cP}$                            | -1.5436 | -0.0508 | -0.0478 | 0.0975  | 0.0021   |
| $G^{*E}/\text{J mol}^{-1}$                    | -1609.3 | -1279.5 | -288.3  | 278.1   | 4.1      |
| Cyclohexane + 2-butanol at 303.15 K           |         |         |         |         |          |
| $V^E/\text{cm}^3 \text{ mol}^{-1}$            | 2.6076  | 0.9382  | 0.4843  | 0.2154  | 0.0055   |
| $\eta^E/\text{cP}$                            | -2.6827 | 1.1618  | -0.7633 | 0.3605  | 0.0031   |
| $G^{*E}/\text{J mol}^{-1}$                    | -3565.4 | 56.9    | -161.4  | 56.3    | 5.7      |
| Cyclohexane + 2-methyl-1-propanol at 303.15 K |         |         |         |         |          |
| $V^E/\text{cm}^3 \text{ mol}^{-1}$            | 1.3414  | 0.9822  | 0.5622  | 0.0445  | 0.0029   |
| $\eta^E/\text{cP}$                            | -2.5065 | 0.4703  | -0.0246 | -0.0020 | 0.0025   |
| $G^{*E}/\text{J mol}^{-1}$                    | -2218.9 | -1171.8 | 64.7    | 273.3   | 5.4      |
| Cyclohexane + 2-methyl-2-propanol at 303.15 K |         |         |         |         |          |
| $V^E/\text{cm}^3 \text{ mol}^{-1}$            | 3.2745  | -0.6154 | 0.1878  | 0.1912  | 0.0044   |
| $\eta^E/\text{cP}$                            | -4.1136 | 2.8885  | -2.5558 | +1.4511 | 0.0110   |
| $G^{*E}/\text{J mol}^{-1}$                    | -4537.5 | 2011.8  | -984.2  | -397.4  | 6.4      |
| Cyclohexane + 1-butanol at 313.15 K           |         |         |         |         |          |
| $V^E/\text{cm}^3 \text{ mol}^{-1}$            | 1.7217  | 0.5843  | 0.6219  | 0.8384  | 0.0032   |
| $\eta^E/\text{cP}$                            | -1.1656 | -0.0211 | -0.0353 | 0.0454  | 0.0027   |
| $G^{*E}/\text{J mol}^{-1}$                    | -1660.6 | -1141.3 | -127.3  | 345.7   | 3.6      |
| Cyclohexane + 2-butanol at 313.15 K           |         |         |         |         |          |
| $V^E/\text{cm}^3 \text{ mol}^{-1}$            | 2.9859  | 0.9987  | 0.3088  | 0.3491  | 0.0032   |
| $\eta^E/\text{cP}$                            | -1.7332 | 0.7162  | -0.4634 | 0.1155  | 0.0021   |
| $G^{*E}/\text{J mol}^{-1}$                    | -3241.2 | 228.1   | -219.2  | -221.5  | 5.9      |
| Cyclohexane + 2-methyl-1-propanol at 313.15 K |         |         |         |         |          |
| $V^E/\text{cm}^3 \text{ mol}^{-1}$            | 1.6230  | 1.0126  | 0.4953  | -0.0757 | 0.0040   |
| $\eta^E/\text{cP}$                            | -1.7510 | 0.3707  | -0.0155 | -0.1019 | 0.0026   |
| $G^{*E}/\text{J mol}^{-1}$                    | -2216.7 | -821.1  | 131.4   | -33.2   | 6.5      |
| Cyclohexane + 2-methyl-2-propanol at 313.15 K |         |         |         |         |          |
| $V^E/\text{cm}^3 \text{ mol}^{-1}$            | 3.3983  | -0.3726 | 0.1040  | 0.1208  | 0.0089   |
| $\eta^E/\text{cP}$                            | -2.1566 | 1.3429  | -1.1848 | 0.5381  | 0.0047   |
| $G^{*E}/\text{J mol}^{-1}$                    | -3600.0 | 1384.1  | -993.2  | -311.9  | 4.8      |

systems in which at least one of the components exhibits association, and where solute-solvent complexes have not been formed or have low stability. Cyclohexane is a non polar liquid with a remarkable power for the disruption of the molecular order mainly due to his cyclic structure that takes up rather volume. For a given temperature,

the breaking is much larger as the branching of the atom of C which carries the OH group increases. When  $T$  increases, the values on  $\eta^E$  and  $G^{*E}$  become less negative. Similar behaviour can be observed in other systems previously studied in our laboratory<sup>1,2,5</sup>. For the mixtures with 1-butanol, we propose that other effects, such as interstitial arrangement, must be taken into account.

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