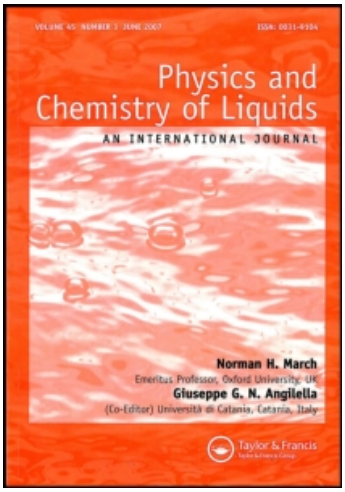

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Dynamic Viscosity and Excess Volume of the Ternary Heptane Methylcyclohexane 1-Methylnaphtalene Versus Composition and Temperature

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To cite this Article Dauge, P. , Boned, C. , Baylaucq, A. and Jose, J.(1998) 'Dynamic Viscosity and Excess Volume of the Ternary Heptane Methylcyclohexane 1-Methylnaphtalene Versus Composition and Temperature', Physics and Chemistry of Liquids, 36: 3, 163 — 177
To link to this Article: DOI: 10.1080/00319109808030607
URL: http://dx.doi.org/10.1080/00319109808030607

Phys. Chem. Liq., 1998, Vol. 36, pp. 163–177
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DYNAMIC VISCOSITY AND EXCESS VOLUME OF THE TERNARY HEPTANE + METHYLCYCLOHEXANE + 1-METHYLNAPHTALENE VERSUS COMPOSITION AND TEMPERATURE

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(Received 20 May 1997)

The density ρ and the dynamic viscosity η of the ternary mixture heptane + methylcyclohexane + 1-methylnaphtalene were measured at 303.15, 323.15 and 343.15 K at atmospheric pressure for molar fractions x_i = 0, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875 and 1 (with $\sum_{i=1}^{3} x_i = 1$). The experimental data for η and ρ (135 values) can be used to evaluate the excess volume V^E and the excess energy of activation for viscous flow ΔG^E. The density is modelled over the entire experimental domain of composition and temperature with an absolute average deviation of 0.03% and the dynamic viscosity with an absolute average deviation of 0.7%.

Keywords: Viscosity; excess energy of activation for viscous flow; ternary mixtures; hydrocarbons

1. INTRODUCTION

In the study of a mixture, excess properties such as the excess volume V^E, or the excess viscosity η^E or the excess energy of activation for viscous flow ΔG^E provide indications on the intermolecular interactions between the different components of the mixture. A number of studies have already been made on binary mixtures with a wide variety of components. These include, for example, alcohol + methylacetate

mixtures [1], mixtures made up of aromatics compounds [2], mixtures with water [3], mixtures of linear [4] or non-linear [5] alkanes, or alcohol and alkane mixtures [6] etc. The reader will find very varied systems in references [7 – 17], but these examples only represent a small part of the work already carried out on binaries. However there are far fewer studies on the excess properties of ternary mixtures. A few results have been published recently: ternaries with aromatics compounds [2], water + ethanol + 2-methoxy-2-methylbutane [3], butylamine + cyclohexane + benzene [18], tributylamine + cyclohexane + benzene [18], trifluoroethanol + water + tetraethylene glycol dimethyl ether [19, 20], acetone + isooctane + toluene [21]. The interest of studying ternary mixtures is first of all to provide experimental data which can then be used, on the basis of information on the three associated binaries or of a general knowledge of the system, to develop models representative of ternary systems. These models could then possibly be generalized to multi-component systems with more than three components, or to other ternary systems with different components. The problem is theoretically complex: it has been shown that when a third component is added to a binary system major modifications may occur. Even if the molecules are themselves only slightly polar, if they are very different they can form complexes with very different polarities. Various models are proposed, but as it has already been emphasized elsewhere [18] experimental measurements of excess quantities in ternary mixtures are very rare, which makes it difficult to confront the results provided by the different equations used in the models with experimental data.

In this paper we present data for the ternary heptane + methylcyclohexane + 1-methylnaphtalene. One of the interesting features of this system is that it can simulate [22], in certain conditions, the C_5^+ fraction (fraction including hydrocarbons with 5 or more carbon atoms) of certain petroleum fluids. This system was studied here versus composition so as to cover the entire ternary diagram, but also versus temperature, which yields a more interesting data base.

2. EXPERIMENTAL TECHNIQUES

Apparatus

The density ρ is determined with the aid of an Anton-Paar DMA 60 resonance densitometer. Error on temperature T is estimated at ± 0.05 K

and error on ρ is ± 0.03 kg.m^{-3}(depending on authors [5, 6, 8, 10, 11, 14, 18, 19, 21], with this apparatus the accuracy varies between $\pm$ 0.001 kg.m^{-3}and $\pm$ 0.05 kg.m^{-3}). The kinematic viscosity ν is determined using a classical capillary viscometer. Several KPG tubes, connected to a Lauda S/1 Viscotimer semi-automatic analyser, were used. The error on T is $\pm$ 0.1 K. After multiplication by the density ρ, the dynamic viscosity η is obtained with a relative uncertainty lower than 1%.

Characteristics of the Samples

The substances used are commercially available chemicals with the following degrees of purity: heptane (Aldrich, purity > 99%, molecular weight M = 100.205 g.mol^{-1}), methylcyclohexane (Aldrich, purity > 99.5%, M = 98.189 g.mol^{-1}), 1-methylnaphtalene (Aldrich purity > 98%, M = 142.201 g.mol^{-1}). The viscosity of 1-methylnaphtalene is much higher than that of the other substances whatever the temperature may be. For example, at T = 303.15 K the viscosity of heptane is 370 μPa.s, that of methylcyclohexane 638.7 μPa.s and that of 1-methylnaphtalene 2617 μPa.s. For this reason the two binaries containing the 1-methylnaphtalene are highly contrasted. The mixtures are prepared by weighing at room temperature to obtain the molar fractions x_1, x_2, x_3, with $\sum_{i=1}^{3} x_i = 1$. (subscript 1 for heptane, 2 for methylcyclohexane and 3 for 1-methylnaphtalene).

3. EXPERIMENTAL RESULTS

The dynamic viscosity η and the density ρ were studied at 303.15, 323.15 and 343.15 K. The composition varies such that x_i = 0, 0.125, 0.25, 0.375, 0.50, 0.625, 0.75, 0.875 and 1 with $\sum_{i=1}^{3} x_i = 1$. There are therefore 9 values for pure substances, 63 for the three binaries and 63 for the ternary proper.The mixture is therefore described by 126 data relative to $\eta(T, x_i)$ and $\rho(T, x_i)$. Results are presented in Table I. Figure 1 represents the surface $\eta(x_1, x_2, x_3)$ at T = 323.15 K in ternary representation and Figure 2 corresponds to $\rho(x_1, x_2, x_3)$ in the same conditions.

TABLE I Variations of dynamic viscosity η and density ρ versus temperature and composition ($x_{1\text{-methylnaphtalene}} = 1 - x_{\text{heptane}} - x_{\text{methylcyclohexane}}$)

		303.15 K		*323.15 K*		*343.15 K*	
x_{heptane}	$x_{\text{methylcyclo}}$	ρ ($kg.m^{-3}$)	η ($\mu Pa.s$)	ρ($kg.m^{-3}$)	η ($\mu Pa.s$)	ρ($kg.m^{-3}$)	η ($\mu Pa.s$)
0.125	0.125	944.24	1500	928.66	1100	913.02	869
0.250	0.125	901.37	1120	885.55	848	869.46	671
0.375	0.125	858.53	870	842.36	677	825.77	545
0.500	0.125	815.23	693	798.71	547	781.96	449
0.625	0.125	772.02	560	755.38	451	738.08	372
0.750	0.125	728.85	462	711.59	377	694.02	312
0.125	0.250	913.53	1220	897.65	911	881.74	715
0.250	0.250	870.18	934	853.90	718	837.49	575
0.375	0.250	826.37	737	809.86	580	793.12	471
0.500	0.250	782.76	594	766.07	476	748.84	393
0.625	0.250	739.29	490	722.26	396	704.60	327
0.125	0.375	882.32	991	865.94	758	849.54	602
0.250	0.375	838.27	797	821.71	622	805.15	503
0.375	0.375	794.32	652	777.25	518	760.14	423
0.500	0.375	749.96	521	732.78	421	715.40	347
0.125	0.500	850.18	870	833.57	672	817.02	543
0.250	0.500	805.55	684	788.71	540	771.56	439
0.375	0.500	760.75	559	743.67	447	726.20	368
0.125	0.625	817.18	748	800.38	585	783.30	474
0.250	0.625	771.80	600	754.73	477	737.22	391
0.125	0.750	783.25	684	766.07	551	748.63	455
1.000	0.000	676.00	370	658.43	303	640.33	252
0.875	0.125	686.44	389	667.98	317	649.95	263
0.750	0.250	695.50	411	677.80	335	659.80	277
0.625	0.375	707.07	436	687.90	354	669.91	292
0.500	0.500	717.10	465	698.22	375	680.30	309
0.375	0.625	727.08	498	708.81	400	690.96	328
0.250	0.750	737.60	538	719.67	430	701.84	350
0.125	0.875	748.56	585	730.87	466	713.05	377
0.000	1.000	760.39	639	742.50	501	724.64	405
0.875	0.000	717.53	438	701.39	357	683.78	295
0.750	0.000	760.39	524	744.22	424	726.85	350
0.625	0.000	803.28	644	787.25	512	770.26	418
0.500	0.000	846.70	800	830.36	625	813.72	503
0.375	0.000	889.65	1030	873.23	781	857.13	621
0.250	0.000	931.77	1360	916.08	1000	900.40	783
0.125	0.000	974.08	1840	958.53	1300	943.15	981
0.000	0.000	1015.43	2620	1000.62	1750	985.75	1270
0.000	0.125	986.47	2060	971.37	1440	956.11	1080
0.000	0.250	956.90	1670	941.40	1200	925.80	929
0.000	0.375	926.33	1370	910.33	1010	894.18	791
0.000	0.500	894.82	1130	878.60	853	861.96	673
0.000	0.625	862.33	972	845.72	733	828.76	584
0.000	0.750	829.07	829	812.03	640	794.86	513
0.000	0.875	795.06	715	777.64	559	760.26	450

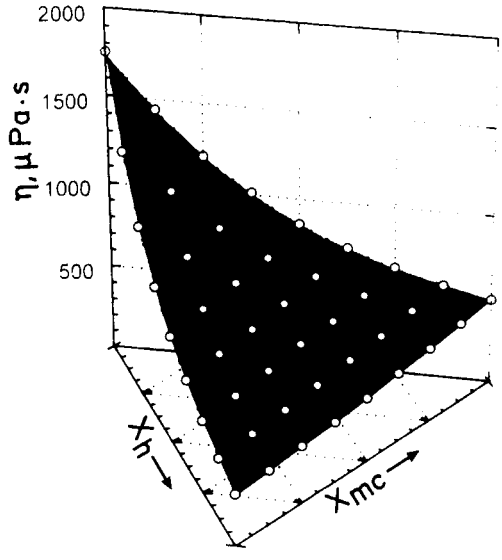

FIGURE 1 Variations of dynamic viscosity η at T = 323.15 K versus composition (molar fraction) in the ternary diagram.

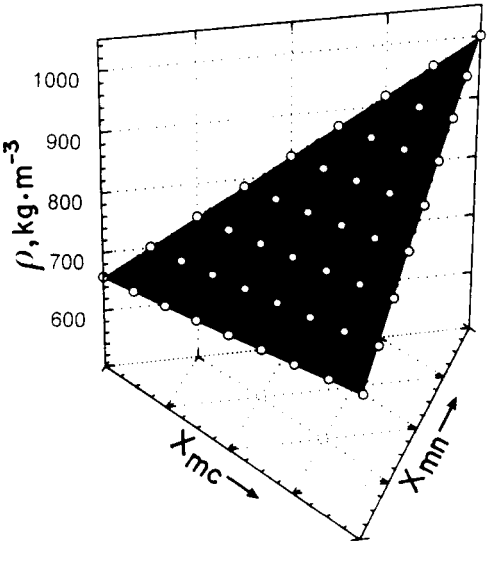

FIGURE 2 Variations of density ρ at T = 323.15 K versus composition (molar fraction) in the ternary diagram.

4. DISCUSSION

Viscosity and Excess Energy of Activation for Viscous Flow

Several empirical or semi-empirical methods have been proposed to model the viscosity of a mixture on the basis of viscosity of pure components. Our purpose here is not to provide an exhaustive review. We will simply indicate that with respect to the so-called mixing rule method a distinction has to be made between rules associated with mixtures assumed to be ideal and those associated with real mixtures. The former involve no adjustable parameter for they contain no term representative of intermolecular interactions; the latter generally involve one or more adjustable parameters as they include with respect to the ideal rules a corrective term, which is believed to represent interactions.

In the framework of ideal rules (this term will be used although is certainly inexact from a thermodynamic point of view) a widely used relationship is that of Grunberg and Nissan [23] which can be demonstrated from very general postulates [24]:

$$\mathrm{Ln}\eta = x_1\mathrm{Ln}\eta_1 + x_2\mathrm{Ln}\eta_2 + x_3\mathrm{Ln}\eta_3 \qquad (1)$$

From the data on pure substances presented in (Tab. I), and given knowledge of the composition of the mixture, its viscosity can be evaluated. To determine the performance of the representation the following quantities are defined:

$$\mathrm{Dev}(i) = 100\left(1 - \frac{\eta_{\mathrm{cal}^{(i)}}}{\eta_{\mathrm{exp}^{(i)}}}\right) \quad DM = \max(|\mathrm{Dev}(i)|)$$

$$\mathrm{AAD} = \frac{1}{N}\sum_{i=1}^{N}|\mathrm{Dev}(i)| \quad \mathrm{Bias} = \frac{1}{N}\sum_{i=1}^{N}\mathrm{Dev}(i)$$

in which N represents the number of data used in the calculation. For mixing rules the pure substances have of course to be excluded, and one thus has $N = 126$ for all three binaries and the ternary, for the three temperatures. The quantity Bias characterises the distribution of points on either side of the theoretical curve, whereas the quantity

AAD characterises the fact that the experimental values are more or less close to the theoretical curve. Finally DM charcterises the maximum relative error introduced by the model. In the case of equation (1) one obtains AAD = 9.46%, DM = 22.9 % and Bias = −9.46% (all the points are below the theoretical curve).

Another theoretically justified relationship is that known as the Katti and Chaudhri relationship [25] . Because its base is more physical than equation (1), it could be thought to give a better representation of the ideal behaviour. For a ternary it is expressed in the form:

$$\mathrm{Ln}(\eta V) = x_1 \mathrm{Ln}(\eta_1 V_1) + x_2 \mathrm{Ln}(\eta_2 V_2) + x_3 \mathrm{Ln}(\eta_3 V_3) \qquad (2)$$

in which V is the molar volume ($V_i = M_i/\rho_i$ with M_i the molar mass of component i and $M = \sum_{i=1}^{3} x_i M_i$ for the mixture). This calculation gives AAD = 9.76%, DM = 23.7% and Bias = −9.76%. This relationship can be deduced from Eyring's representation of dynamic viscosity of a pure fluid [26]. The calculation leads to:

$$\mathrm{Ln}(\eta V) = x_1 \mathrm{Ln}(\eta_1 V_1) + x_2 \mathrm{Ln}(\eta_2 V_2) + x_3 \mathrm{Ln}(\eta_3 V_3) + \frac{\Delta G^E}{RT} \qquad (3)$$

in which R is the constant of the perfect gases and ΔG^E the excess energy of activation for viscous flow. This term ΔG^E appears in the calculation as representative of a deviation with respect to the ideality and if $\Delta G^E = 0$, we return to equation (2). From the data in Table I, it is possible to determine the values of ΔG^E. Figure 3 represents variations of ΔG^E versus composition in the ternary diagram at T = 323.15 K. It will be observed that for the three binaries ΔG^E is negative (this is also true for the other temperatures). For the binary heptane + methylcyclohexane the minimum is less clearly marked than for the binaries heptane + 1-methylnaphtalene and methylcyclohexane + 1-methylnaphtalene. We have already indicated that these last two binaries are more contrasted than the heptane + methylcyclohexane system in the sense that the ratio η_i/η_j of the viscosities of the two substances is more different from 1. The more interactions there are, the more the value of the minimum is clearly marked. Figure 4 represents variations of ΔG^E versus T for $x_2 = 0.25$ (methylcyclohexane) and for values of the molar fraction x_1 of

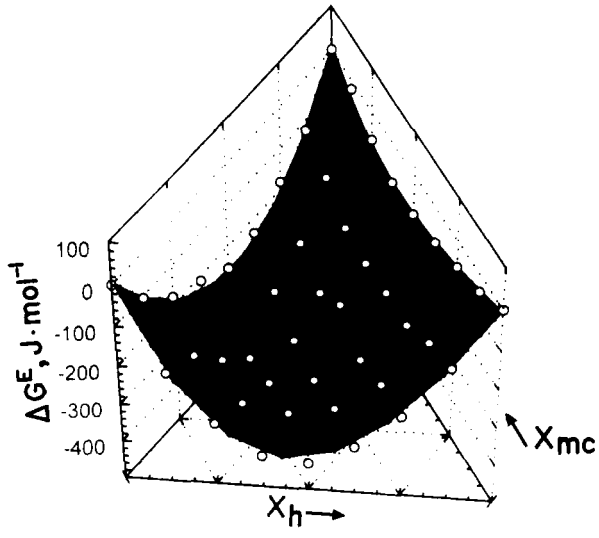

FIGURE 3 Variations of the excess energy of activation for viscous flow ΔG^E at T = 323 K versus composition (molar fraction) in the ternary diagram.

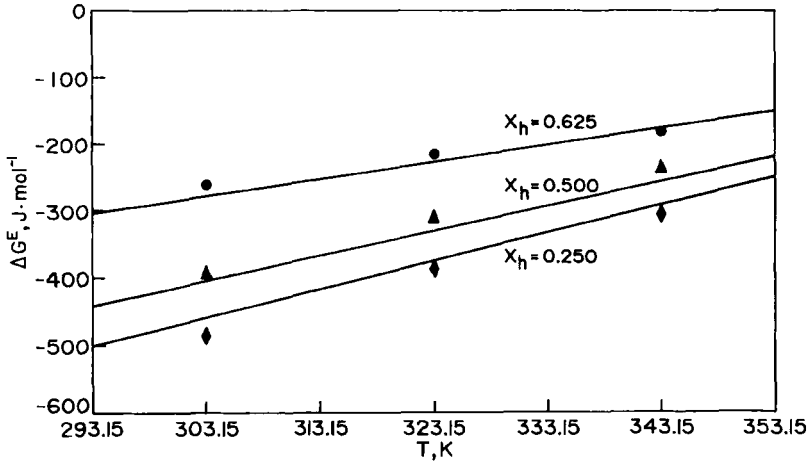

FIGURE 4 Variations versus T of the excess energy of activation for viscous flow ΔG^E for x(methylcyclohexane) = 0.250 and for x(heptane) = 0.250, 0.500 and 0.625 (— curves calculated with equation (9)).

heptane: 0.250, 0.500 and 0.625. The viscous flow excess activation free energy ΔG^E is an increasing function of T. The slope seems to be slightly dependent of the value of x_1. Finally Figure 5 represents values

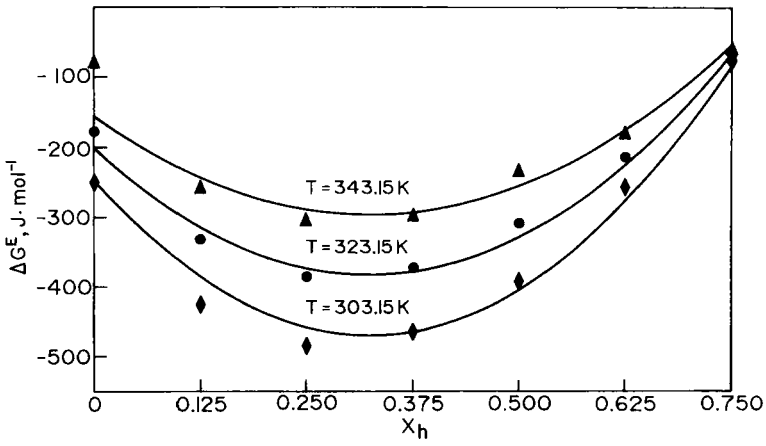

FIGURE 5 Variations versus x(heptane) at x(methylcyclohexane) = 0.250 of the excess energy of activation for viscous flow ΔG^E, for various temperatures (— curves calculated with equation (9)).

of ΔG^E versus x_1 (heptane) at $x_2 = 0.25$ (methylcyclohexane), for the three temperatures.

For the real binary mixtures, Katti and Chandhri [25] proposed the expression $\Delta G^E = x_1 x_2 W$ in which W is an adjustable parameter. In exactly the same way, for the Grunberg and Nissan equation, the corrective term $x_1 x_2 d$ is added. Thus for a ternary one has the generalised relationships:

$$\mathrm{Ln}\eta = x_1 \mathrm{Ln}\eta_1 + x_2 \mathrm{Ln}\eta_2 + x_3 \mathrm{Ln}\eta_3 + (x_1x_2 + x_1x_3 + x_2x_3)d \quad (4)$$

$$\mathrm{Ln}(\eta V) = x_1 \mathrm{Ln}(\eta_1 V_1) + x_2 \mathrm{Ln}(\eta_2 V_2) + x_3 \mathrm{Ln}(\eta_3 V_3) + (x_1x_2 + x_1x_3 + x_2x_3)\frac{W}{RT} \quad (5)$$

For equation (4), AAD = 3.27%, Bias = −0.51% and DM = 12.4% with $d = -0.36242$, and for equation (5), AAD = 3.15%, Bias = −0.55% and DM = 12.3% with W = −997.266 J.mol^{-1}. In the two previous equations (4) and (5), the terms W and d, which characterize the amplitude of binary interactions, intervene symmetrically for each of the binaries. Figure 3 shows that this is certainly

not the case. So each binary interaction is introduced independently, writing:

$$\mathrm{Ln}\eta = x_1\mathrm{Ln}\eta_1 + x_2\mathrm{Ln}\eta_2 + x_3\mathrm{Ln}\eta_3 + (d_{12}x_1x_2 + d_{13}x_1x_3 + d_{23}x_2x_3) \tag{6}$$

$$\mathrm{Ln}(\eta V) = x_1\mathrm{Ln}(\eta_1 V_1) + x_2\mathrm{Ln}(\eta_2 V_2) + x_3\mathrm{Ln}(\eta_3 V_3) + (w_{12}x_1x_2 + w_{13}x_1x_3 + w_{23}x_2x_3)/RT \tag{7}$$

For the generalised Grunberg-Nissan relationship (equation (6)), the calculation yields AAD = 2.12%, Bias = −0.14% and DM = 8.7% with $d_{12} = -0.14654$, $d_{13} = -0.60916$ and $d_{23} = -0.37263$. For the generalised Katti and Chaudhri relationship (equation (7)) the calculation gives AAD = 1.70%, Bias = 0.025%, DM = 7.44% with $w_{12} = -398.65$ J. mol^{-1}, $w_{13} = -1719.04$ J.mol^{-1}and $w_{23} = -1053.13$ J.mol^{-1}. It will be noted that $|d_{12}| < |d_{23}| < |d_{13}|$ and $|w_{12}| < |w_{23}| < |w_{13}|$ which corresponds to the order of amplitude of binary interactions indicated by Figure 3. However equation (7) does not take into account of the fact that ΔG^E increases with temperature T, apparently in a linear fashion according to Figure 4 (or equivalent figures plotted for other conditions of composition). Thus one can write:

$$\mathrm{Ln}(\eta V) = x_1\mathrm{Ln}(\eta_1 V_1) + x_2\mathrm{Ln}(\eta_2 V_2) + x_3\mathrm{Ln}(\eta_3 V_3) + (w_{12}x_1x_2 + w_{13}x_1x_3 + w_{23}x_2x_3)\frac{(1+\alpha T)}{RT} \tag{8}$$

which gives AAD = 0.81%, Bias = 0.02%, DM = 5.1% with $w_{12} = -1501.15$ J.mol^{-1}, $w_{13} = -6569.11$ J.mol^{-1} and $w_{23} = -4055.06$ J.mol^{-1} and $\alpha = -0.0022932$ K^{-1} (the w_{ij} being < 0, the fact that $\alpha < 0$ reflects the fact that ΔG^E increases with T). In this last relationship there are only binary-type interaction terms of the form $w_{ij}x_ix_j$. It is certain that a ternary-type interaction term $w_{123}x_1x_2x_3$ has to be taken into account, corresponding to the formulation:

$$\mathrm{Ln}(\eta V) = x_1\mathrm{Ln}(\eta_1 V_1) + x_2\mathrm{Ln}(\eta_2 V_2) + x_3\mathrm{Ln}(\eta_3 V_3) + (w_{12}x_1x_2 + w_{13}x_1x_3 + w_{23}x_2x_3 + w_{123}x_1x_2x_3)\frac{(1+\alpha T)}{RT} \tag{9}$$

In this last case the Absolute Average Deviation on dynamic viscosity is AAD = 0.72% with Bias = 0.06% and DM = 4.05%. It should be indicated that the correlation coefficient between the calculated and experimental values is 0.99963. The values of the coefficients are $w_{12} = -1733.85\,\text{J.mol}^{-1}$, $w_{13} = -7708.60\,\text{J.mol}^{-1}$, $w_{23} = -5025.08\,\text{J.mol}^{-1}$, $w_{123} = -1286.10\,\text{J.mol}^{-1}$, $\alpha = -0.0024300\ \text{K}^{-1}$. One still has $|w_{12}| < |w_{23}| < |w_{13}|$. It will be noted that w_{123} is of the same order of magnitude as w_{12}, which seems to indicate that ternary interaction is not negligible compared with binary interaction. But the contribution of $w_{123}x_1x_2x_3$ is limited by the fact that $x_1x_2x_3$ has a maximum value of 0.037 obtained for $x_i = x_j = x_k = 1/3$, while the term x_ix_j then has the value 0.11. Hence the contribution of the ternary interaction term remains nonetheless less significant than the contributions of the binary interaction terms. It should be stressed that the value of AAD is of the order of magnitude of experimental uncertainty on η, and in these conditions it is pointless to try and obtain a better representation. Also, an equation of the Redlich-Kister type is of course able to provide a satisfactory representation of variations of ΔG^E of the ternary versus composition, as has already been established for other ternaries [2, 3]. But the number of adjustment parameters is greater. For example in the case of the water + ethanol + 2-methoxy-2-methylbutane system [3] there are seven parameters for the ternary interaction term $x_1x_2x_3$ alone, and four parameters for each of the binary terms x_ix_j, i.e. a total of 19 adjustable parameters. Moreover the temperature-dependence of ΔG^E is not taken into account as the study was carried out at 298.15 K.

For certain authors [7, 12] the fact that the excess viscosity is negative (in other words in this case $\Delta G^E < 0$) means that the predominant effect during mixing is the breaking up of the ordered structures present in the pure liquids. Other authors [1, 6] interpret the negative values of ΔG^E by the fact that it is the repulsive forces of interaction which predominate, therefore corresponding to the breaking of bonds within the ordered structures. We will see below that the excess volumes V^E are also negative, which corresponds to a reduction in the free volume, which tends to increase viscosity, i.e. to increase ΔG^E. So the increasing disorder linked to the breaking of ordered structures has a greater effect on viscosity than reduction of the free volume.

Density and Excess Molar Volume

The excess molar volume V^E is defined by $\rho = M/(\sum_{i=1}^{3} x_i V_i + V^E)$ with $M = \sum_{i=1}^{3} x_i M_i$ the equivalent molar mass of the liquid and $V_i = M_i/\rho_i$ the molar volume of component i. Thus:

$$V^E = \sum_{i=1}^{3} \frac{x_i M_i}{\rho} - \sum_{i=1}^{3} \frac{x_i M_i}{\rho_i}$$

Figure 6 represents variations of V^E versus composition, in the ternary diagram, at T = 323.15 K. The shape is the same for the other two temperatures. The excess volume is negative with a very clearly marked minimum for the binary heptane + 1-methylnaphtalene and a very slightly marked minimum for the binary heptane + methylcyclohexane. The negative values of V^E indicate that in all cases the free volume is reduced. Figure 7 shows variations of V^E versus temperature for $x_2 = 0.25$ (methylcyclohexane) and for values of the molar fraction of heptane $x_1 = 0.25$, 0.625 and 0.75. V^E is observed to decrease with T, i.e. $|V^E|$ is observed to increase. Finally Figure 8 represents variations

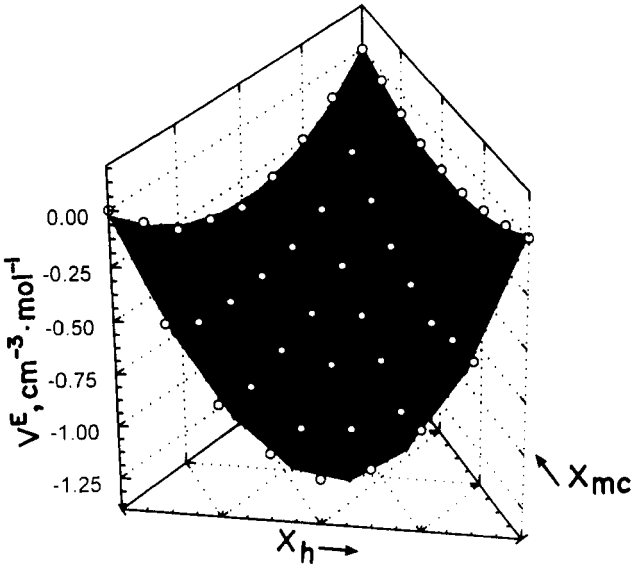

FIGURE 6 Variations of the excess volume V^E at T = 323.15 K versus composition (molar fraction) in the ternary diagram.

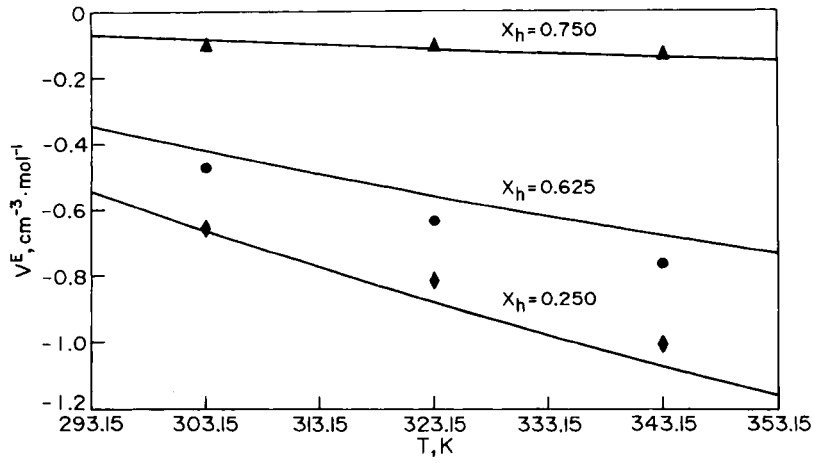

FIGURE 7 Variations versus T of the excess volume V^E for x (methylcyclohexane) = 0.250 and for x (heptane) = 0.250, 0.625 and 0.750 (— curves calculated with equation (10)).

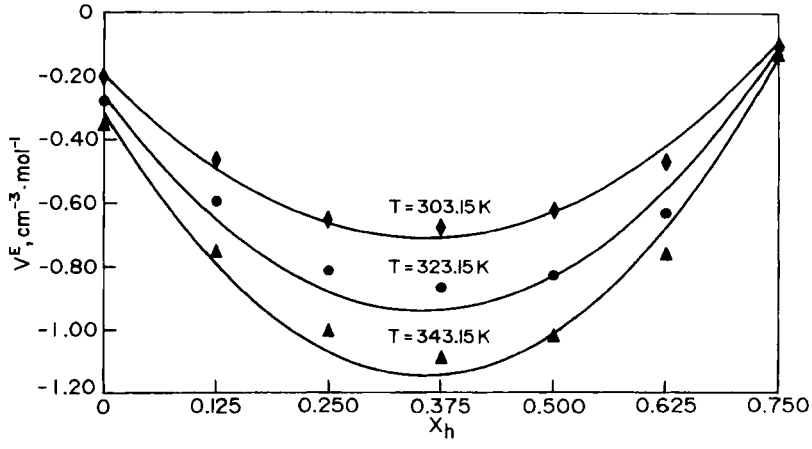

FIGURE 8 Variations versus x (heptane) at x (methylcyclohexane) = 0.250 of the excess volume V^E for various temperatures (—curves calculated with equation (10)).

of V^E versus x_1 (heptane) at $x_2 = 0.25$ (methylcyclohexane) for the three temperatures.

If the density ρ is represented by $\rho = \sum_{i=1}^{3} x_i M_i / \sum_{i=1}^{3} x_i V_i$ in other words without taking account of the contraction of the free volume, the following values are obtained for Absolute Average Deviation on

ρ:AAD = 0.39%, Bias = 0.39% (since $\rho_{cal} < \rho_{exp}$ in all cases), DM = 0.95% with a correlation coefficient of 0.9990. To account for the term V^E, following the same approach as for ΔG^E, we propose to represent it by:

$$V^E = (V_{12}x_1x_2 + V_{13}x_1x_3 + V_{23}x_2x_3 + V_{123}x_1x_2x_3)\left(1 + \frac{\alpha}{T}\right) \quad (10)$$

Thus, for ρ, the following values were obtained: AAD = 0.027%, Bias = 0.007%, DM = 0.22% with a correlation coefficient of 0.999993. The values of the parameters are $V_{12} = -2.89209$ cm^3. mol^{-1}, $V_{13} = -22.4286$ cm^3. mol^{-1}, $V_{23} = -6.55349$ cm^3. mol^{-1}, $V_{123} = -11.5489$ cm^3. mol^{-1}, and $\alpha = -254.839$ K. Thus $|V_{12}| < |V_{23}| < |V_{13}|$, which is consistent with the order of amplitudes of binary interactions deduced from Figure 6. It will be noted here that the term V_{123} is large and so $x_1x_2x_3|V_{123}|$ for $x_1 = x_2 = x_3 = 1/3$ is higher than $x_1x_2|V_{12}|$ which means that the ternary interaction term has a significant influence on V^E.

It is of course possible to improve representation of ρ by increasing the number of adjustment parameters. Equally variation with T is represented very schematically. If an adjustment is made at fixed temperature (and so with 4 parameters) a significant improvement is observed. Moreover if, at fixed temperature, the study is limited to one of the three binaries, ρ can be represented with one single interaction parameter with AAD = 0.005%, a value very close to experimental uncertainty. This is characteristic and indicates that the global representation of interactions for the whole system, on the one hand, and the rule chosen to represent variations of V^E versus temperature, on the other hand, are too simple to account for the complexity of the phenomenon.

References

[1] Acevedo, I. L., Postigo, M. A. and Katz, M. (1990). *Phys. Chem. Liq.*, **21**, 87.
[2] Aminabhavi, J. M. and Joshi, S. S. (1992). *Ind. J. Technology*, **30**, 197.
[3] Arce, A., Blanco, A., Martinez-Ageitos, J. Mendoza, J. and Soto, A. (1996). In *CHISA'96 12th International Congress of Chemical and Process Engineering, Praha*, P.3. 174 (401).
[4] Aucejo, A., Burguet, M. C., Munoz, R. and Marques, J. L. (1995). *J. Chem. Eng. Data*, **40**, 141.
[5] Awwad, A. L. and Salman, M. A. (1986). *Fluid Phase Equilibria*, **31**, 105.
[6] Bravo, R., Pintos, M., Amigo, A. and Garcia, M. (1991). *Phys. Chem. Liq.*, **22**, 245.

[7] Cea, P., Lafuente, C., Morand, J. P., Royo, F. M. and Urieta, J. S. (1995). *Phys. Chem. Liq.*, **29**, 69.
[8] De Lorenzi, L., Fermeglia, M. and Torriano, G. (1995). *J. Chem. Eng. Data*, **40**, 1172.
[9] Dusart, O., Pieparski, C., Pieparski, S. and Viallard, A. (1976). *Journal de Chimie Physique*, **73**, 837.
[10] Esteve, X., Boer, D., Patil, K. R., Chaudhari, S. K. and Coronas, A. (1994). *J. Chem. Eng. Data.*, **39**, 767.
[11] Franjo, C., Jimenez, E., Iglesias, T. P., Legido, J. L. and Andrade, P. A. (1995). *J. Chem. Eng. Data*, **40**, 68.
[12] Heric, E. L. and Brewer, J. G. (1967). *J. Chem. Eng. Data*, **12**, 574.
[13] Matsuo, S. and Makita, T. (1991). *Int. J. Thermophys.*, **12**, 459.
[14] Papaioannou, D. and Panayiotou, C. (1995). *J. Chem. Eng. Data*, **40**, 202.
[15] Riggio, R., Martinez, H. E., De Salas, N. Z., De Toigo, M. D. and Ramos, J. F. (1995). *Can. J. Chem.*, **73**, 1274.
[16] Sastry, N. V. and Raj, M. M. (1995). *Phys. Chem. Liq.*, **30**, 47.
[17] El-Banna, M. M. (1997). *J. Chem. Eng. Data*, **42**, 31.
[18] Oswal, S. L. and Patel, S. G. (1994). *J. Chem. Soc. Faraday Trans.*, **90**, 1083.
[19] Olive, F., Patil, K. R., Fernandez, J. and Coronas, A. (1995). *Termochim. Acta*, **259**, 57.
[20] Olive, F., Chaudhari, S. K., Patil, K. R. and Coronas, A. (1996). *Can. J. Chem. Eng.*, **74**, 163.
[21] Mamagakis, N. and Panayiotou, C. (1989). *Zeitschrift für Physikalische Chemie Neue Folge*, **162**, 57
[22] Baylaucq, A., Daugé, P. and Boned, C. (1997). *Int. J. Thermophys.* (in press).
[23] Grunberg, L. and Nissan, A. H. (1949). *Nature*, **164**, 799.
[24] Lichtenecker, K. and Rother, K. (1931). *Physikalische Zeitschrift*, **32**, 255.
[25] Katti, P. K. and Chaudhri, M. M. (1964). *J. Chem. Eng. Data*, **9**, 442.
[26] Glasstone, S. , Laidler, K. J. and Eyring, H. (1941). *The Theory of Rate Processes*, (McGraw Hill, New York).