International Journal of Thermophysics, Vol. 19, No. 5, 1998

Viscosity and Density at High Pressures in an Associative Ternary

C. Boned,[1,2] M. Moha-Ouchane,[1,3] A. Allal,[4] and M. Benseddik[3]

Received February 19, 1998

The dynamic viscosity η and the density ρ of the associative ternary mixture water + diacetone alcohol + 2-propanol have been measured as a function of temperature T (303.15, 323.15, and 343.15 K) and pressure P ($\leqslant 100$ MPa). The experimental results correspond to 698 values of η and ρ. With reference to the 54 values previously published on pure substances and 486 values for three corresponding binaries, the system is globally described by 1188 experimental values for various values of P, T and composition. The results for η are discussed in terms of excess activation energy of viscous flow.

KEY WORDS: density; excess activation energy of viscous flow; high pressure; ternary mixture; viscosity.

1. INTRODUCTION

As we have indicated in previous articles [1, 2], while there is a substantial volume of data describing variations of the dynamic viscosity η of fluids versus temperature at atmospheric pressure, studies of variations versus pressure are less common, especially for mixtures, and particularly for systems where nonmonotonic viscosity behavior versus composition can be noted. This occurs when interactions between the solvents are important. The viscosity moves through a maximum or minimum (at fixed temperature T and pressure P) when the composition is varied. As for mixtures, there are very few studies versus pressure (see, for example, Ref. 2). Some data

[1] Laboratoire Haute Pression, Centre Universitaire de Recherche Scientifique, Avenue de l'Université, 64000 Pau, France.
[2] To whom correspondence should be adressed.
[3] Département de Physique, Faculté des Sciences Dhar el Mahrez, Fes, Maroc.
[4] Laboratoire de Physique des Matériaux Industriels, Centre Universitaire de Recherche Scientifique, Avenue de l'Université, 64000 Pau, France.

0195-928X/98/0900-1325$15.00/0

concerning binaries are now available, but there are practically no systematic studies concerning ternary mixtures.

In a previous paper [2] we selected the water + 4-hydroxy-4-methyl-2-pentanone (or diacetone alcohol, abbreviated DAA) + 2-propanol mixture. The dynamic viscosity η and density ρ of the pure substances and the three corresponding binaries (involving 54 values for the pure substances and 486 for the binaries) have already been published [2]. This paper extends the study to cover the ternary under the same pressure and temperature conditions as for the pure substances and binaries, with a sufficient range of composition to provide complete coverage of the representative ternary diagram.

2. EXPERIMENTAL PROCEDURE

2.1. Apparatus

The viscosity η was determined with the aid of a falling-body viscometer, technical details of which are provided in Ref. 3. Values of the density ρ for pressures between 0.1 and 70 MPa were measured with an Anton-Paar DMA60 + DMA 601 resonance densimeter with an additional 512P cell. The values were extrapolated to $P = 100$ MPa according to the procedure described in Ref. 3. The uncertainty in the temperature T was estimated at ± 0.5 K for measurements of η, and the uncertainty in temperature for density ρ was ± 0.05 K. The uncertainty in the pressure P was estimated at ± 0.05 MPa for the measurements of ρ and ± 0.1 MPa for the measurements of η (except at $P = 0.1$ MPa). The uncertainty in the density ρ was less than 0.1 $kg \cdot m^{-3}$ (except at $P = 0.1$ MPa, where it was estimated to be below 0.03 $kg \cdot m^{-3}$) which corresponds to the estimate made by Papaioannou et al. [4] who use an identical approach (with a 512 cell limited to 40 MPa, instead of the more recent 512P cell limited to 70 MPa). The uncertainty in viscosity η was of the order of 2%. As already discussed previously [1–3, 5, 6], this error is comparable with that obtained by other authors for similar experimental systems. The interested reader will find comparative curves for heptane and methylcyclohexane in Ref. 6, and for water and 2-propanol in Ref. 2, which contain plots of our values and of those obtained by other authors. As an example, in the case of pure water, Fig. 1 shows η versus pressure at $T = 303.15$ K for our measurements [2] and those of different authors [7, 8] and Fig. 2 shows values for the deviation $\Delta\eta = 100(\eta_{exp} - \eta_{calc})/\eta_{exp}$, with $\eta_{calc} = a + bP + cP^2$. It should be pointed out that at atmospheric pressure the kinematic viscosity η/ρ was determined with a classical capillary viscometer. For this purpose, several KGP tubes, connected to a semi-automatic S/1 Lauda analyzer,

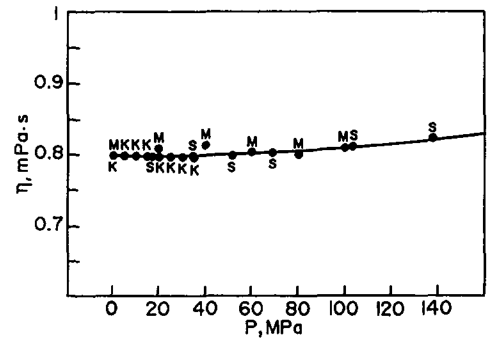

Fig. 1. Dynamic viscosity η of water versus pressure at $T = 303.15$ K ($-\eta = a + bP + cP^2$). *K*, Ref. 7; *S*, Ref. 8; *M*, the present work, Ref. 2.

were used. In this case, the uncertainty in the temperature was ± 0.01 K. After multiplying by ρ, the dynamic viscosity η was obtained with an uncertainty of less than 1%.

2.2. Characteristics of Samples

The water (H_2O, molar mass $M = 18.015\ \mathrm{g \cdot mol^{-1}}$) is distilled water. The two other substances are commercially available chemicals with the following purity levels: DAA ($C_6H_{12}O_2$: Interchim, purity > 99%, molar mass $M = 113.13\ \mathrm{g \cdot mol^{-1}}$) and 2-propanol ($C_3H_8O$: Sigma-Aldrich, purity > 99.5%, molar mass $M = 60.1\ \mathrm{g \cdot mol^{-1}}$). The mixtures were prepared by weighing at atmospheric pressure and ambient temperature to obtain the molar fractions $x_i = 0.1$, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9

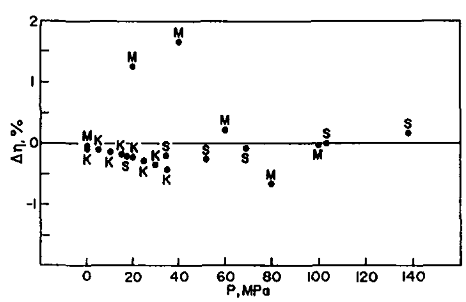

Fig. 2. Deviation $\Delta\eta$ of the literature data for the viscosity of water from the equation: $\eta = a + bP + cP^2$ ($T = 303.15$ K). *K*, Ref. 7; *S*, Ref. 8; *M*, the present work, Ref. 2.

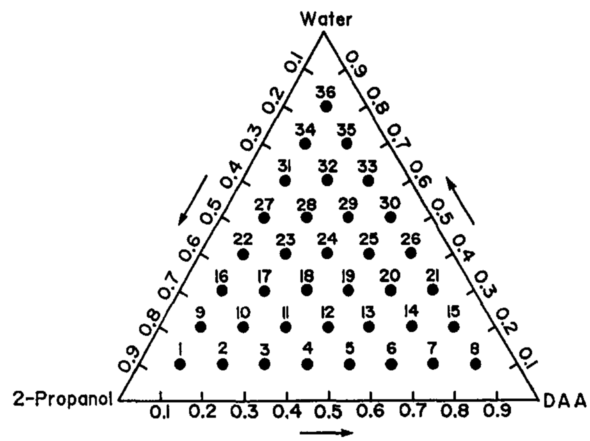

Fig. 3. Points representative of the three pure substances, the three binaries, and the ternary in the ternary diagram (versus mole fraction).

(x_w: water, x_d: DAA, x_p: 2-propanol and $x_w + x_d + x_p = 1$) corresponding to the 36 points of the ternary diagram shown in Fig. 3. We recall that the systems associated with the three summits (pure substances) and the three sides (binaries) have already been studied [2]. The samples were studied immediately after their preparation in order to prevent absorption from the ambient air. The pure fluids, not degassed, were stored in hermetically sealed bottles. The samples were in the liquid state within the experimental temperature and pressure domain.

3. RESULTS

Measurements of the dynamic viscosity η were made at 303.15, 323.15, and 343.15 K and at 0.1, 20, 40, 60, 80, and 100 MPa. A total of 648 values was obtained for η. Measurement of density was carried out at pressures from 0.1 MPa to 65 MPa in 5 MPa steps. There are 1512 experimental values for ρ. Moreover, values of ρ extrapolated to 80 and 100 MPa with the aid of a Tait-type relationship [3] are also indicated (216 values). However, in order to reduce the amount of tabulated data, we retain only those temperatures and pressures for which viscosity has been measured. Additional density data (1080 values) will be published soon in Ref. 9. Table I presents the values measured as a function of P, T, and composition expressed as a mole fraction (x_w, x_p, $x_d \neq 0$ and 1). Figures 4 and 5 represent variations of ρ as a function of P (for different T) and as a function of T (for different P) in the case corresponding to point 19 on the

Table I. Dynamic Viscosity η and Density ρ for the Ternary Mixture

			303.15 K		323.15 K		343.15 K	
P (MPa)	x_p[a]	x_d[b]	ρ ($kg \cdot m^{-3}$)	η ($\mu Pa \cdot s$)	ρ ($kg \cdot m^{-3}$)	η ($\mu Pa \cdot s$)	ρ ($kg \cdot m^{-3}$)	η ($\mu Pa \cdot s$)
0.1	0.1	0.1	951.9	3080	934.9	1730	917.1	1050
20	0.1	0.1	961.4	3350	945.3	1870	928.7	1170
40	0.1	0.1	970.2	3640	954.8	1970	938.9	1240
60	0.1	0.1	978.3	3940	963.6	2090	948.3	1320
80	0.1	0.1	985.6	4270	974.6	2220	956.9	1400
100	0.1	0.1	992.6	4610	985.1	2390	964.7	1520
0.1	0.1	0.2	948.3	3930	933.4	2060	912.0	1230
20	0.1	0.2	958.6	4300	941.8	2290	924.6	1400
40	0.1	0.2	968.0	4790	952.1	2540	935.7	1560
60	0.1	0.2	976.5	5370	961.4	2820	945.8	1690
80	0.1	0.2	984.4	5880	971.3	3070	955.0	1830
100	0.1	0.2	991.7	6450	981.3	3280	963.3	1980
0.1	0.1	0.3	944.7	4260	926.4	2180	907.4	1300
20	0.1	0.3	955.7	4820	938.5	2490	921.0	1510
40	0.1	0.3	965.6	5460	949.4	2820	932.8	1700
60	0.1	0.3	974.5	6120	959.0	3130	943.2	1900
80	0.1	0.3	982.7	6780	967.9	3520	952.6	2110
100	0.1	0.3	990.2	7560	976.1	3930	961.1	2380
0.1	0.1	0.4	939.6	4160	921.1	2170	902.2	1290
20	0.1	0.4	951.1	4780	934.0	2520	916.4	1510
40	0.1	0.4	961.4	5580	945.2	2890	928.7	1730
60	0.1	0.4	970.8	6400	955.4	3330	939.7	1970
80	0.1	0.4	979.3	7310	964.5	3740	949.5	2220
100	0.1	0.4	987.1	8360	973.0	4220	958.5	2480
0.1	0.1	0.5	935.2	3830	916.6	2080	897.7	1240
20	0.1	0.5	947.3	4490	930.0	2430	912.6	1460
40	0.1	0.5	958.0	5300	941.7	2810	925.4	1690
60	0.1	0.5	967.5	6210	952.1	3260	936.8	1940
80	0.1	0.5	976.2	7230	961.4	3690	946.8	2210
100	0.1	0.5	984.1	8320	969.9	4250	955.9	2500
0.1	0.1	0.6	930.5	3430	912.0	1940	893.1	1180
20	0.1	0.6	943.0	4140	925.8	2280	908.6	1400
40	0.1	0.6	954.0	4970	937.9	2690	921.8	1660
60	0.1	0.6	963.8	5850	948.7	3140	933.4	1910
80	0.1	0.6	972.9	6890	958.4	3590	943.8	2200
100	0.1	0.6	981.1	8070	967.3	4160	953.2	2510
0.1	0.1	0.7	926.9	3050	908.4	1780	889.7	1130
20	0.1	0.7	939.8	3730	922.6	2100	905.7	1350
40	0.1	0.7	951.2	4470	935.1	2500	919.3	1580
60	0.1	0.7	961.4	5310	946.1	2940	931.3	1840
80	0.1	0.7	970.5	6280	955.9	3430	941.8	2130
100	0.1	0.7	979.0	7390	964.8	3930	951.3	2450
0.1	0.1	0.8	923.5	2720	904.9	1630	886.4	1080
20	0.1	0.8	936.7	3250	919.7	1930	902.9	1260

Table I. *(Continued)*

			303.15 K		323.15 K		343.15 K	
P (MPa)	x_p[a]	x_d[b]	ρ $(kg \cdot m^{-3})$	η $(\mu Pa \cdot s)$	ρ $(kg \cdot m^{-3})$	η $(\mu Pa \cdot s)$	ρ $(kg \cdot m^{-3})$	η $(\mu Pa \cdot s)$
40	0.1	0.8	948.5	3890	932.4	2290	916.8	1490
60	0.1	0.8	958.8	4640	943.7	2710	928.9	1760
80	0.1	0.8	968.1	5410	953.6	3140	939.7	2060
100	0.1	0.8	976.6	6530	962.7	3630	949.4	2400
0.1	0.2	0.1	918.1	3300	900.3	1720	881.5	1050
20	0.2	0.1	928.8	3450	912.0	1900	894.8	1180
40	0.2	0.1	938.5	3780	922.6	2080	906.2	1300
60	0.2	0.1	947.2	4140	932.1	2280	916.4	1400
80	0.2	0.1	955.2	4540	940.7	2450	925.4	1490
100	0.2	0.1	962.6	4880	948.6	2580	933.6	1620
0.1	0.2	0.2	920.4	3650	902.1	1910	883.1	1150
20	0.2	0.2	931.6	4060	914.6	2190	897.1	1330
40	0.2	0.2	941.8	4610	925.7	2430	909.2	1490
60	0.2	0.2	950.9	5130	935.6	2700	919.9	1660
80	0.2	0.2	959.1	5650	944.5	2970	929.5	1830
100	0.2	0.2	966.7	6260	952.7	3260	938.3	2030
0.1	0.2	0.3	920.2	3660	901.7	1960	882.6	1170
20	0.2	0.3	932.0	4170	914.8	2290	897.3	1350
40	0.2	0.3	942.5	4840	926.3	2540	909.8	1560
60	0.2	0.3	951.9	5420	936.6	2930	921.0	1760
80	0.2	0.3	960.6	6280	945.8	3280	930.9	1970
100	0.2	0.3	968.5	7240	954.2	3640	939.9	2180
0.1	0.2	0.4	918.5	3470	900.0	1910	881.2	1140
20	0.2	0.4	930.9	4060	913.6	2200	896.5	1330
40	0.2	0.4	942.1	4760	925.7	2570	909.7	1560
60	0.2	0.4	952.1	5560	936.5	2950	921.2	1780
80	0.2	0.4	961.2	6440	946.2	3310	931.6	2010
100	0.2	0.4	969.6	7410	955.1	3760	941.0	2260
0.1	0.2	0.5	916.7	3190	898.2	1800	879.1	1100
20	0.2	0.5	929.5	3740	912.3	2080	895.0	1270
40	0.2	0.5	940.6	4450	924.6	2430	908.4	1490
60	0.2	0.5	950.6	5250	935.5	2800	920.2	1720
80	0.2	0.5	959.6	6140	945.2	3220	930.6	1970
100	0.2	0.5	967.9	7110	954.1	3700	940.1	2240
0.1	0.2	0.6	914.2	2880	895.9	1670	876.9	1060
20	0.2	0.6	927.3	3470	910.4	1950	893.2	1240
40	0.2	0.6	938.7	4130	923.0	2300	906.9	1450
60	0.2	0.6	949.0	4900	934.1	2680	919.0	1680
80	0.2	0.6	958.1	5720	944.1	3080	929.6	1920
100	0.2	0.6	966.4	6680	953.1	3580	939.2	2200
0.1	0.2	0.7	912.2	2590	893.6	1540	874.8	1020
20	0.2	0.7	925.7	3050	908.6	1830	891.8	1190
40	0.2	0.7	937.5	3660	921.6	2170	905.8	1410
60	0.2	0.7	948.0	4370	933.0	2540	918.1	1650

Table I. *(Continued)*

			303.15 K		323.15 K		343.15 K	
P (MPa)	x_p[a]	x_d[b]	ρ ($kg \cdot m^{-3}$)	η (μ Pa · s)	ρ ($kg \cdot m^{-3}$)	η (μ Pa · s)	ρ ($kg \cdot m^{-3}$)	η (μ Pa · s)
80	0.2	0.7	957.4	5140	943.1	2950	928.6	1910
100	0.2	0.7	966.0	6070	952.3	3420	938.1	2170
0.1	0.3	0.1	890.7	3070	872.5	1650	853.3	1000
20	0.3	0.1	902.6	3310	885.5	1840	868.0	1120
40	0.3	0.1	913.0	3690	897.0	2030	880.4	1260
60	0.3	0.1	922.4	4220	907.2	2260	891.5	1390
80	0.3	0.1	930.9	4650	916.3	2430	901.3	1530
100	0.3	0.1	938.6	5150	924.7	2620	910.2	1650
0.1	0.3	0.2	896.7	3200	878.1	1740	858.7	1040
20	0.3	0.2	908.8	3590	891.6	2000	873.9	1200
40	0.3	0.2	919.6	4110	903.4	2220	886.9	1370
60	0.3	0.2	929.2	4580	913.9	2510	898.3	1540
80	0.3	0.2	938.0	5250	923.2	2820	908.4	1710
100	0.3	0.2	946.0	6070	931.7	3120	917.6	1880
0.1	0.3	0.3	899.9	3110	881.2	1730	861.8	1020
20	0.3	0.3	912.5	3660	895.2	2030	877.6	1220
40	0.3	0.3	923.7	4280	907.4	2310	890.9	1440
60	0.3	0.3	933.5	4840	918.1	2600	902.6	1640
80	0.3	0.3	942.4	5680	927.6	3000	913.0	1840
100	0.3	0.3	950.5	6500	936.3	3400	922.3	2040
0.1	0.3	0.4	900.4	2910	881.7	1660	862.3	1000
20	0.3	0.4	913.4	3450	896.1	1930	878.6	1190
40	0.3	0.4	924.8	4070	908.5	2250	892.2	1410
60	0.3	0.4	934.8	4720	919.5	2580	904.2	1600
80	0.3	0.4	943.9	5510	929.3	2970	914.7	1820
100	0.3	0.4	952.2	6340	938.1	3410	924.1	2060
0.1	0.3	0.5	900.4	2690	881.8	1580	862.8	986
20	0.3	0.5	913.7	3180	896.6	1820	879.6	1160
40	0.3	0.5	925.4	3780	909.4	2140	893.5	1360
60	0.3	0.5	935.7	4470	920.7	2490	905.7	1560
80	0.3	0.5	945.0	5220	930.7	2890	916.5	1770
100	0.3	0.5	953.4	6070	939.9	3350	926.1	2030
0.1	0.3	0.6	899.8	2460	881.0	1480	862.0	970
20	0.3	0.6	913.5	2940	896.4	1720	879.2	1140
40	0.3	0.6	925.4	3420	909.5	2020	893.5	1320
60	0.3	0.6	936.0	4110	921.0	2360	906.0	1520
80	0.3	0.6	945.5	4820	931.2	2740	916.9	1760
100	0.3	0.6	954.2	5680	940.4	3170	926.7	2020
0.1	0.4	0.1	868.9	2710	850.3	1510	830.7	927
20	0.4	0.1	881.6	3030	864.5	1680	846.8	1050
40	0.4	0.1	892.6	3420	876.6	1910	860.1	1180
60	0.4	0.1	902.5	3850	887.4	2100	871.8	1330
80	0.4	0.1	911.4	4260	896.9	2360	882.0	1460
100	0.4	0.1	919.5	4840	905.6	2640	891.1	1600

Table I. *(Continued)*

			303.15 K		323.15 K		343.15 K	
P (MPa)	x_p [a]	x_d [b]	ρ ($kg \cdot m^{-3}$)	η ($\mu Pa \cdot s$)	ρ ($kg \cdot m^{-3}$)	η ($\mu Pa \cdot s$)	ρ ($kg \cdot m^{-3}$)	η ($\mu Pa \cdot s$)
0.1	0.4	0.2	876.9	2730	858.1	1550	838.5	966
20	0.4	0.2	889.8	3200	872.5	1800	854.9	1110
40	0.4	0.2	901.1	3670	885.0	2090	868.4	1270
60	0.4	0.2	911.2	4260	896.0	2360	880.4	1430
80	0.4	0.2	920.2	4840	905.7	2620	890.9	1610
100	0.4	0.2	928.5	5480	914.5	2930	900.2	1830
0.1	0.4	0.3	882.0	2670	863.2	1530	843.5	967
20	0.4	0.3	895.2	3180	877.9	1790	860.3	1120
40	0.4	0.3	906.8	3720	890.8	2090	874.3	1290
60	0.4	0.3	917.4	4290	901.8	2390	886.5	1470
80	0.4	0.3	926.9	4980	911.9	2750	897.0	1660
100	0.4	0.3	935.6	5730	920.9	3110	906.5	1880
0.1	0.4	0.4	884.6	2480	865.9	1460	846.4	946
20	0.4	0.4	898.3	2960	881.1	1720	863.6	1090
40	0.4	0.4	910.1	3510	894.1	2000	877.9	1280
60	0.4	0.4	920.5	4140	905.5	2320	890.2	1470
80	0.4	0.4	929.9	4780	915.7	2680	901.1	1660
100	0.4	0.4	938.5	5540	924.9	3060	910.8	1890
0.1	0.4	0.5	885.9	2370	867.3	1380	848.0	915
20	0.4	0.5	899.9	2760	882.9	1630	865.6	1070
40	0.4	0.5	912.0	3210	896.1	1910	880.1	1240
60	0.4	0.5	922.6	3820	907.7	2230	892.7	1440
80	0.4	0.5	932.1	4460	918.0	2560	903.7	1660
100	0.4	0.5	940.7	5190	927.2	2960	913.6	1900
0.1	0.5	0.1	850.5	2430	831.9	1360	812.2	858
20	0.5	0.1	864.0	2820	846.9	1600	829.3	994
40	0.5	0.1	875.7	3140	859.8	1820	843.3	1140
60	0.5	0.1	886.0	3660	871.0	2070	855.6	1280
80	0.5	0.1	895.2	4060	880.9	2320	866.3	1430
100	0.5	0.1	903.5	4590	889.9	2520	875.8	1590
0.1	0.5	0.2	860.5	2410	841.7	1380	821.9	854
20	0.5	0.2	874.2	2810	857.0	1600	839.4	1010
40	0.5	0.2	886.0	3260	870.1	1850	853.8	1180
60	0.5	0.2	896.5	3740	881.5	2100	866.2	1340
80	0.5	0.2	905.8	4300	891.6	2400	877.0	1510
100	0.5	0.2	914.2	4870	900.8	2710	886.7	1700
0.1	0.5	0.3	866.7	2300	848.1	1370	828.4	835
20	0.5	0.3	880.6	2760	863.6	1580	846.0	1000
40	0.5	0.3	892.5	3260	876.9	1830	860.6	1180
60	0.5	0.3	903.1	3840	888.5	2100	873.2	1360
80	0.5	0.3	912.7	4390	898.7	2390	884.2	1540
100	0.5	0.3	921.3	5080	907.8	2770	894.0	1750
0.1	0.5	0.4	870.4	2220	851.7	1310	832.3	821
20	0.5	0.4	884.7	2590	867.6	1520	850.3	990

Table I. *(Continued)*

			303.15 K		323.15 K		343.15 K	
P (MPa)	x_p[a]	x_d[b]	ρ $(kg \cdot m^{-3})$	η $(\mu Pa \cdot s)$	ρ $(kg \cdot m^{-3})$	η $(\mu Pa \cdot s)$	ρ $(kg \cdot m^{-3})$	η $(\mu Pa \cdot s)$
40	0.5	0.4	896.9	3000	881.2	1780	865.1	1170
60	0.5	0.4	907.7	3580	893.0	2080	877.8	1360
80	0.5	0.4	917.3	4170	903.4	2370	888.9	1560
100	0.5	0.4	926.0	4810	912.8	2760	898.8	1780
0.1	0.6	0.1	836.1	2130	817.2	1260	797.3	766
20	0.6	0.1	850.3	2490	833.2	1440	815.5	916
40	0.6	0.1	862.5	2860	846.6	1650	830.3	1060
60	0.6	0.1	873.2	3280	858.2	1860	843.0	1210
80	0.6	0.1	882.7	3730	868.6	2090	853.9	1360
100	0.6	0.1	891.3	4180	877.8	2370	863.7	1530
0.1	0.6	0.2	846.3	2110	827.5	1260	807.5	764
20	0.6	0.2	860.6	2510	843.7	1480	825.9	927
40	0.6	0.2	872.8	2960	857.2	1710	840.9	1080
60	0.6	0.2	883.7	3440	869.0	1980	853.7	1260
80	0.6	0.2	893.4	3930	879.3	2260	864.8	1420
100	0.6	0.2	902.1	4510	888.5	2560	874.6	1610
0.1	0.6	0.3	853.0	2090	834.2	1250	814.6	763
20	0.6	0.3	867.5	2440	850.6	1490	833.3	933
40	0.6	0.3	880.1	2860	864.3	1740	848.3	1100
60	0.6	0.3	892.1	3330	876.2	2000	861.3	1280
80	0.6	0.3	900.6	3880	886.7	2300	872.6	1470
100	0.6	0.3	909.3	4430	896.1	2600	882.6	1670
0.1	0.7	0.1	822.8	1960	804.3	1170	784.0	696
20	0.7	0.1	837.5	2300	820.8	1370	802.9	852
40	0.7	0.1	850.0	2710	834.7	1580	818.1	1000
60	0.7	0.1	861.0	3120	846.6	1830	831.1	1160
80	0.7	0.1	870.6	3560	857.0	2080	842.4	1310
100	0.7	0.1	879.3	4060	866.4	2340	852.4	1480
0.1	0.7	0.2	833.5	1960	814.6	1170	794.9	709
20	0.7	0.2	848.4	2300	831.4	1380	814.1	877
40	0.7	0.2	861.1	2680	845.5	1610	829.6	1040
60	0.7	0.2	872.2	3150	857.6	1860	842.6	1210
80	0.7	0.2	882.0	3630	868.3	2110	853.9	1380
100	0.7	0.2	890.9	4150	878.0	2400	863.9	1560
0.1	0.8	0.1	811.1	1850	792.5	1090	772.5	662
20	0.8	0.1	826.6	2160	809.8	1320	792.5	818
40	0.8	0.1	839.6	2550	824.3	1520	808.4	971
60	0.8	0.1	850.9	2970	836.5	1770	821.7	1130
80	0.8	0.1	860.8	3410	847.3	2000	833.3	1290
100	0.8	0.1	869.7	3880	856.9	2250	843.4	1480

[a] x_p, mole fraction of 2-propanol.
[b] x_d, mole fraction of diacetone alcohol.

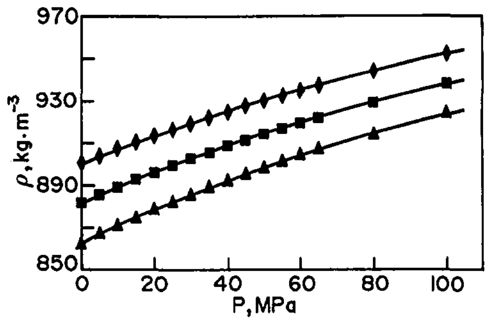

Fig. 4. Density ρ versus pressure P at various temperatures T, for composition $x_w = 0.3$, $x_d = 0.4$, $x_p = 0.3$ (◆: 303.15 K, ■: 323.15 K, ▲: 343.15 K).

ternary diagram in Fig. 3 ($x_w = 0.3$, $x_d = 0.4$, $x_p = 0.3$). Figures 6 and 7 show the dynamic viscosity in the same conditions. Table I and the figures present a general pattern consistent with previous observations made by other authors and by us on pure hydrocarbons or binaries and ternary hydrocarbons. The pressure coefficient of the viscosity variation $(\partial\eta/\partial P)_T$ is positive for all the compositions and the shape of $\eta(P)$ variations shows an increase, while, on the contrary, the temperature variation coefficient $(\partial\eta/\partial T)_P$ is always negative. The group of isotherm and isobar curves is regular. This is also true for density, but in the case of the isotherm a concavity is observed associated with a negative second derivative. This form is compatible with the logarithmic form proposed by Tait to model the influence of pressure on $1/\rho$; this logarithmic form is the one used for

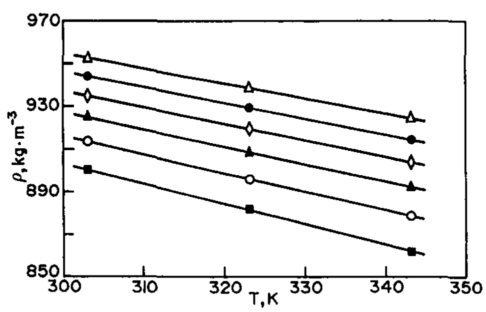

Fig. 5. Density ρ versus temperature T at various pressures P, for composition $x_w = 0.3$, $x_d = 0.4$, $x_p = 0.3$ (■: 0.1 MPa, ○: 20 MPa, ▲: 40 MPa, ◇: 60 MPa, ●: 80 MPa, △: 100 MPa).

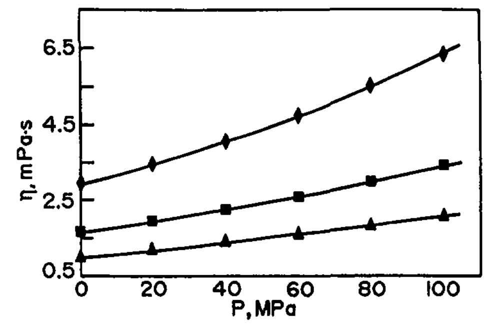

Fig. 6. Dynamic viscosity η versus pressure P at various temperatures T, for composition $x_w = 0.3$, $x_d = 0.4$, $x_p = 0.3$ (♦: 303.15 K, ■: 323.15 K, ▲: 343.15 K).

extrapolation (see, e.g., Ref. 3). It should be noted that variations of ρ versus T are practically linear, but it should be recalled that in the present investigation the temperature variations are very small, the main aim being to observe variations of ρ and η as a function of pressure and the mole fractions of the components.

Figure 8 shows ρ as a function of x_w (water) for constant x_d (diacetone alcohol) at $P = 40$ MPa and $T = 323.15$ K. The variations are not linear, which corresponds to substantial excess volumes (see Ref. 2 for data on excess volume values for the binaries). Figure 9 shows η as a function of x_w for constant x_d at $P = 40$ MPa and $T = 323.15$ K. Points A, B, and C correspond to pure substances and the sides AB, BC, and AC to the

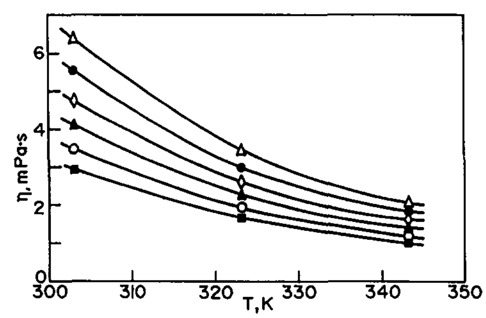

Fig. 7. Dynamic viscosity η versus temperature T at various pressures P, for composition $x_w = 0.3$, $x_d = 0.4$, $x_p = 0.3$ (■: 0.1 MPa, ○: 20 MPa, ▲: 40 MPa, ◇: 60 MPa, ●: 80 MPa, △: 100 MPa).

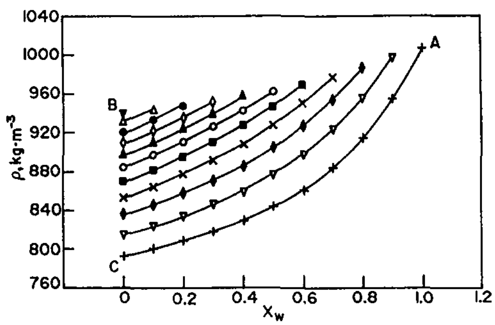

Fig. 8. Density ρ versus x_w (water content) for various x_d (diacetone content) at $P = 40$ MPa and $T = 323.15$ K. (+: $x_d = 0$, ▽: 0.1, ◆: 0.2, ×: 0.3, ■: 0.4, ○: 0.5, ▲: 0.6, ◇: 0.7, ●: 0.8, △: 0.9, ▼: 1).

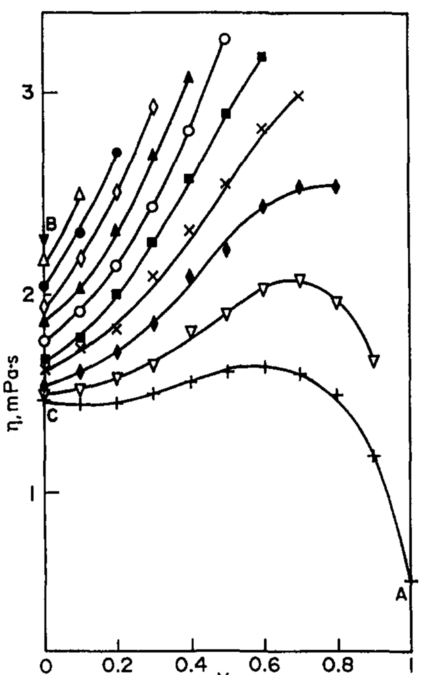

Fig. 9. Dynamic viscosity η versus x_w (water content) at $P = 40$ MPa and $T = 323.15$ K. (+: $x_d = 0$, ▽: 0.1, ◆: 0.2, ×: 0.3, ■: 0.4, ○: 0.5, ▲: 0.6, ◇: 0.7, ●: 0.8, △: 0.9, ▼: 1).

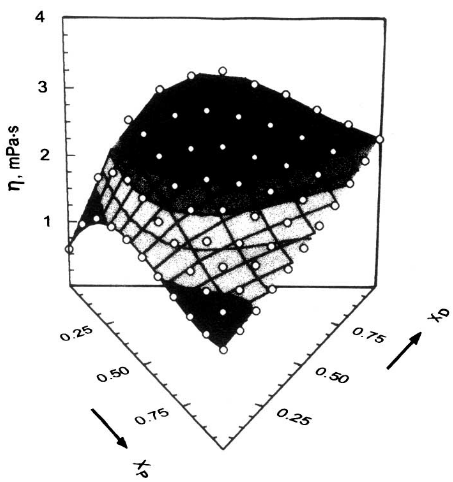

Fig. 10. Surface $\eta(x_w, x_d, x_p)$ in the ternary diagram at $P = 40$ MPa and $T = 323.15$ K.

binaries (to complete the figures we used the data on the pure substances and binaries given in Ref. 2). Figure 10 shows the surface $\eta(x_w, x_d, x_p)$ in the ternary diagram at the same conditions. Finally, Fig. 11 represents the isodynamic viscosity lines in the ternary diagram at $P = 0.1$ MPa and $T = 303.15$ K.

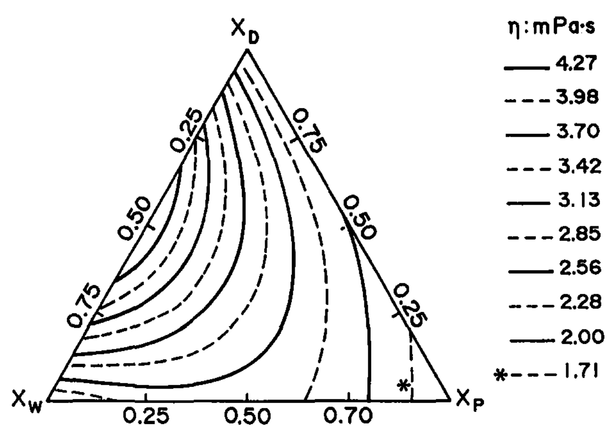

Fig. 11. Isodynamic viscosity lines in the ternary diagram at $P = 0.1$ MPa and $T = 303.15$ K.

4. DISCUSSION

The data obtained on the ternary mixture in the course of this investigation, combined with those obtained previously [2] on the three pure substances and the three binaries, represent a total of 1188 experimental points which can be used to test different representative models incorporating the effects of temperature, pressure, and composition. A preliminary study was carried out with very different models. In the case of the Grunberg and Nissan mixing rule [10],

$$\ln(\eta) = x_{\mathrm{w}} \ln(\eta_{\mathrm{w}}) + x_{\mathrm{p}} \ln(\eta_{\mathrm{p}}) + x_{\mathrm{d}} \ln(\eta_{\mathrm{d}}) \tag{1}$$

we obtained an absolute average deviation (AAD) of 36.5% and a maximum deviation (MD) of 82%. The model is very simple since there are no adjustable parameters, and only viscosity data for the pure substances are required. But with this relationship the variation of η versus composition is monotonic. The above relationship can be modified by introducing adjustable parameters believed to be representative of the interactions of the system studied. We obtained the following relationship in which a corrective term was added:

$$\begin{aligned}\ln(\eta) = {} & x_{\mathrm{w}} \ln(\eta_{\mathrm{w}}) + x_{\mathrm{p}} \ln(\eta_{\mathrm{p}}) + x_{\mathrm{d}} \ln(\eta_{\mathrm{d}}) \\ & + \frac{(a x_{\mathrm{w}} x_{\mathrm{d}} + b x_{\mathrm{w}} x_{\mathrm{p}} + c x_{\mathrm{p}} x_{\mathrm{d}} + d x_{\mathrm{w}} x_{\mathrm{p}} x_{\mathrm{d}})}{(1 + e x_{\mathrm{w}} + f x_{\mathrm{d}} + g x_{\mathrm{p}})} (1 + k T^{1/2} + iP)\end{aligned} \tag{2}$$

which, by a procedure of minimization on the AAD, provides AAD = 2.7% and MD = 16.4%, which is a very satisfactory result since the AAD is of the same order of magnitude as the experimental error. However, the physical significance of the corrective term is not very clear.

It is more interesting to calculate, from the η and ρ values, the excess activation energy of viscous flow ΔG^{E} which appears in

$$\ln(\eta V) = x_{\mathrm{w}} \ln(\eta_{\mathrm{w}} V_{\mathrm{w}}) + x_{\mathrm{p}} \ln(\eta_{\mathrm{p}} V_{\mathrm{p}}) + x_{\mathrm{d}} \ln(\eta_{\mathrm{d}} V_{\mathrm{d}}) + \Delta G^{\mathrm{E}}/RT \tag{3}$$

where $V_i = M_i/\rho_i$ is the molar volume of the component i (molar weight $\sum x_i M_i$ for the mixture) and R is the gas constant. This relation is a modified form of the equation of Katti and Chaudhri [11] and is theoretically justified by Eyring's representation of the dynamic viscosity of a pure fluid [12]. It is interesting to note here that the quantity ηV is also obtained from the time-correlation expression for shear viscosity [13]. Thus, the quantities ηV and ΔG^{E} have a theoretical background, while the corrective term in Eq. (1) does not. ΔG^{E} can easily be calculated from Table I (and Ref. 2). Figure 12 shows the variations of ΔG^{E} versus P, T in

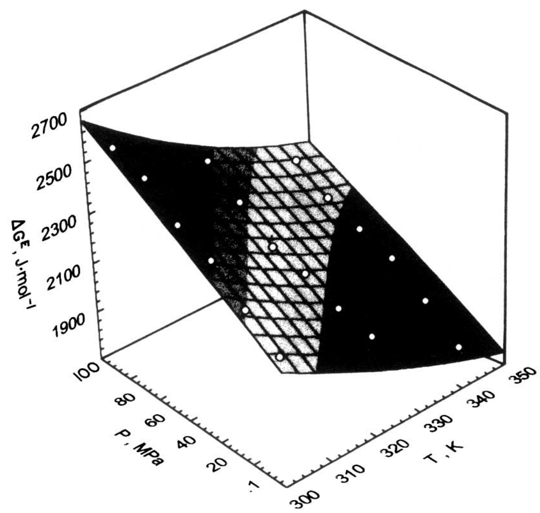

Fig. 12. Variations of $\Delta G^{E}(x_{w}, x_{d}, x_{p})$ versus T and P, for composition $x_{w}=0.3$, $x_{d}=0.4$, $x_{p}=0.3$.

the case corresponding to point 19 on the ternary diagram in Fig. 3 ($x_{w}=0.3$, $x_{d}=0.4$, and $x_{p}=0.3$). Figure 13 shows the surface $\Delta G^{E}(x_{w}, x_{d}, x_{p})$ in the ternary diagram at $P=40$ MPa and $T=323.15$ K. As the system is very associative (except for the binary DAA + 2-propanol), the values of ΔG^{E} are generally very large when water is present in the system. If one

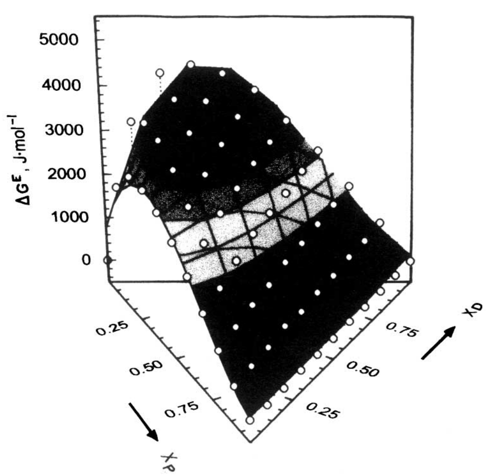

Fig. 13. Surface $\Delta G^{E}(x_{w}, x_{d}, x_{p})$ in the ternary diagram at $P=40$ MPa and $T=323.15$ K.

assumes $\Delta G^{E} = 0$, one obtains AAD = 45.3% and DM = 88.1%. After numerical analysis the representation

$$\Delta G^{E} = \frac{(a'x_w x_d + b'x_w x_p + c'x_p x_d + d'x_w x_p x_d)}{(1 + e'x_w + f'x_d + g'x_p)} (1 + k'T^{1/2} + i'P) \tag{4}$$

gives AAD = 2.34% and DM = 15.5% which is a very good result. Figure 14 shows the variations of the experimental values $\Delta G^{E}{}_{EXP}$ as a function of the calculated values $\Delta G^{E}{}_{CALC}$ obtained in this case. The line corresponds to a linear least squares fit, close to the bisecting line. The calculation gives a correlation factor of 0.9982. The fact that $\Delta G^{E} > 0$ (in other words that the excess viscosity is positive) means it is the attractive forces of interaction which predominate. This is confirmed by the fact that the excess volume V^{E} is negative, which corresponds to a decrease in the free volume, which tends to increase the viscosity, i.e., to increase ΔG_{E} (see previous Ref. 2 for V^{E} in the binaries and Ref. 9 for V^{E} in the ternary).

The models used to account for the viscous behavior versus pressure, temperature, and, in some cases, composition are very varied in their approaches to the problem. The interested reader will find information in Ref. 14. It is interesting to mention the method recently developed by Dymond and Awan [15] and Assael et al. [16], based on the theory of hard spheres, which entails representing viscosity as a function of density. If the coefficients supplied by those authors are used, the results obtained are poor because their adjustment base concerns linear alkanes, but if a new adjustment is performed on the basis of our 1188 values, one obtains AAD = 2.2% and MD = 16.0% which represents very good performance.

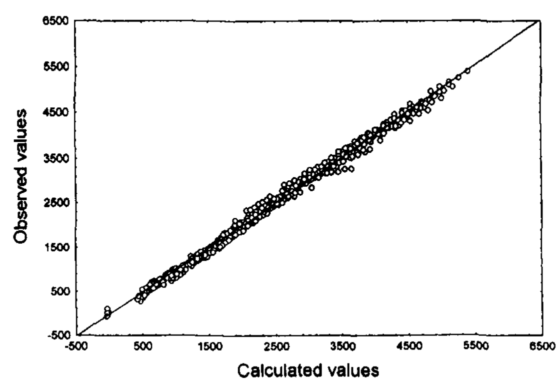

Fig. 14. Variations of the experimental values $\Delta G^{E}{}_{EXP}$ versus the calculated values $\Delta G^{E}{}_{CALC}$ (—: best linear adjustment).

The method mentioned in this investigation, although conceptually different, yields comparable results. Also, an equation of the Redlich–Kister type is able to provide a good representation of the variations of ΔG^{E} of the ternary as a function of composition. But the number of adjustment parameters is greater, and they depend on the pressure and the temperature.

5. CONCLUSION

It is to be hoped that the experimental data supplied in this paper and in the earlier publication [2], which provide a substantial description of variations of η and ρ versus pressure, temperature, and composition, will be included in databases and used to test other models of viscous behavior more sophisticated than those discussed here. The reader is also referred to Refs. 1 and 6 which describe the behavior of viscosity and density as a function of pressure, temperature, and composition of the ternary system heptane + methylcyclohexane + 1-methynaphtalene, which is less associative, and where the variations of η versus composition are only monotonic.

REFERENCES

1. A. Baylaucq, P. Dauge, and C. Boned, *Int. J. Thermophys.* **18**:1089 (1997).
2. M. Moha-Ouchane, C. Boned, A. Allal, and M. Benseddik, *Int. J. Thermophys.* **19**:161 (1998).
3. A. Et-Tahir, C. Boned, B. Lagourette, and P. Xans, *Int. J. Thermophys.* **6**:1309 (1995).
4. D. Papaioannou, M. Bridakis, and C.G. Panayiotou, *J. Chem. Eng. Data* **38**:730 (1993).
5. M. Kanti, B. Lagourette, J. Alliez, and C. Boned, *Fluid Phase Equil.* **64**:291 (1991).
6. A. Baylaucq, C. Boned, P. Dauge, and B. Lagourette, *Int. J. Thermophys.* **18**:3 (1997).
7. J. Kestin, H. E. Khalifa, and R. J. Correia, *J. Phys. Chem. Ref. Data* **10**:71 (1981).
8. E. M. Stanley and R. C. Batten, *J. Phys. Chem.* **73**:1187 (1969).
9. M. Moha-Ouchane, Thèse de Doctorat, (Université de Fès, Maroc, 1999).
10. L. Grunberg and A. H. Nissan, *Nature* **164**:799 (1949).
11. P. K. Katti and M. M. Chaudhri, *J. Chem. Eng. Data* **9**:442 (1964).
12. S. Glasstone, K. J. Laidler, and H. Eyring, in *The Theory of Rate Processes* (McGraw-Hill, New York, 1941).
13. R. Zwanzig, *Ann. Rev. Phys. Chem.* **16**:67 (1965).
14. A. Baylaucq, Thèse de Doctorat (Université de Pau et des Pays de l'Adour, France, 1996).
15. J. H. Dymond and M. A. Awan, *Int. J. Thermophys.* **10**:941 (1989).
16. M. J. Assael, J. H. Dymond, and V. Tselekidou, *Int. J. Thermophys.* **11**:863 (1990).