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Viscosity and Excess Volume at High Pressures in Associative Binaries

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The dynamic viscosity η and the density ρ of three pure substances (water, 2-propanol, diacetone alcohol) and the three associated binaries were measured versus temperature T (303.15, 323.15, and 343.15 K) and pressure P. For the binary systems the mole fractions x of each component were, successively, 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1. For viscosity the experimental results ($P \leqslant 100$ MPa) represent a total of 540 data points: 54 for the pure substances and 486 for the binary mixtures ($x \neq 0$ and $x \neq 1$). For density the experimental results ($P \leqslant 70$ MPa) represent 1260 values: 126 for the pure substances and 1134 for the binary mixtures ($x \neq 0$ and $x \neq 1$). The mixtures with water are highly associative and the curves for the variation of η with composition exhibit a maxima. The variations of the excess activation energy of viscous flow ΔG^{E} are discussed. Moreover, the measurements of ρ are sufficiently accurate to determine the excess volumes V^{E} versus pressure, temperature, and composition.

KEY WORDS: excess activation energy of flow; excess volume; high pressure; viscosity.

1. INTRODUCTION

Knowledge of the dynamic viscosity η of liquid mixtures is of major interest in various research and industrial domains. A great number of reviews and compilations can be found in the literature on this subject. While a large number of results describe the behavior of η versus temperature, there are far fewer studies describing variations versus pressure. It is generally observed

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that the viscosity is markedly influenced by the pressure. Moreover, as regards mixtures, another considerable factor is composition. For many binary mixtures variations of η as a function of composition are monotonic. This occurs when interactions are weak. But in certain cases, when molecular interactions between the two solvents are stronger, nonmonotonic viscosity behavior can be noted, and the viscosity moves through a maximum or a minimum (at fixed temperature and pressure) when the composition varies. For example, for the cyclohexane + methanol system a minimum is observed [1], while for the water + hexane system there is a maximum [1]. Moreover, for a given binary, the presence of the maximum or minimum depends on the P,T conditions of the study. Thus study of η is an important technique to determine the structural changes associated with binary mixtures. It is often the presence of numerous hydrogen bonds which triggers this variation and systematic experimental studies are necessary to advance the theoretical understanding of the relationship among intermolecular forces, the structure of the solution, and its properties. Unfortunately, nonmonotonic systems have most commonly been investigated at atmospheric pressure $P = 0.1$ MPa. Studies versus pressure are rare. We should mention work done on the benzene + cyclohexane system [2] between 0.1 and 29.5 MPa, at 298.15 K, which demonstrates the presence of a minimum, and research conducted on the water + CaCl system [3] between 0.1 and 375 MPa at 298.15 K, which also presents a minimum. On the other hand, both the methanol + *n*-butylamine system and the ethanol + *n*-butylamine system [4] present a maximum, as does the ethanol + propylamine system [5] between 0.1 and 50.8 MPa, once again, at a temperature of 298.15 K.

It therefore seemed of interest to study the influence of pressure (and also temperature) on other systems presenting a viscosity maximum or a viscosity minimum as a function of composition. We chose water + 4-hydroxy-4-methyl-2-pentanone (or diacetone alcohol; DAA) because at atmospheric pressure [6] it exhibits a very clearly marked maximum (at 298.15 K the $\eta_{\text{mixture}}/\eta_{\text{water}}$ ratio $= 6.4$ and the $\eta_{\text{DAA}}/\eta_{\text{water}}$ ratio $= 2.9$, whereas the viscosity of water [7] at the same temperature is $\eta_{\text{water}} = 890.5$ (μPa · s). We also investigated the water + 2-propanol (isopropanol) system, which also presents [8] a marked maximum when studied at 0.1 MPa ($\eta = 3267$ μPa · s at 298.15 K for a mole fraction in water of 0.690; $\eta_{\text{2-propanol}} = 2016$ μPa · s). The viscosity of this binary has also been studied [9] as a function of pressure up to 120 MPa. Moreover, to extend the coverage of our study, we also determined η for the DAA + 2-propanol system, for which interactions are weaker. We shall see that the representative function of η versus composition is monotonic in this case. Let us state here that DAA and its mixtures have been studied rarely. Finally,

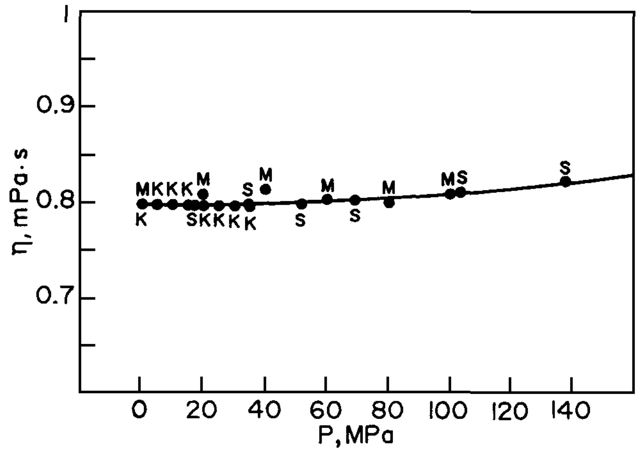

Fig. 1. Viscosity η of water versus pressure at $T = 303.15$ K. K, Ref. 15; S, Ref. 18; M, present paper. (——): $\eta = a + bP + cP^2$.

from the η values, the excess activation energy of flow ΔG^E can be determined and, therefore, its variations versus pressure, temperature, and composition of the mixture.

Another physical parameter which is important and often essential to determine (and model) the viscosity η is the density ρ. When the density is known along isotherms and isobars, the isothermal compressibility coefficient and thermal expansion coefficient of the fluid considered can be

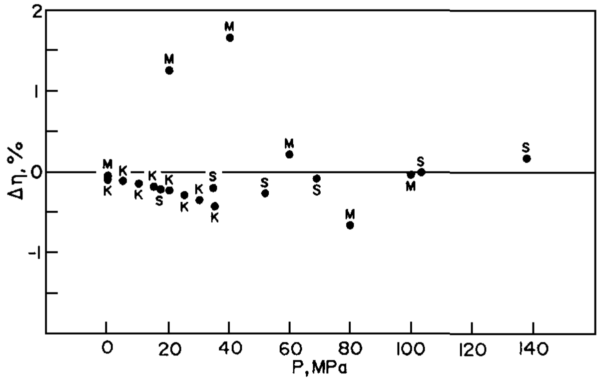

Fig. 2. Deviations $\Delta\eta$ of the literature data for the viscosity of water from the correlation of $\eta = a + bP + cP^2$ ($T = 303.15$ K) K, Ref. 15; S, Ref. 18; M, present paper.

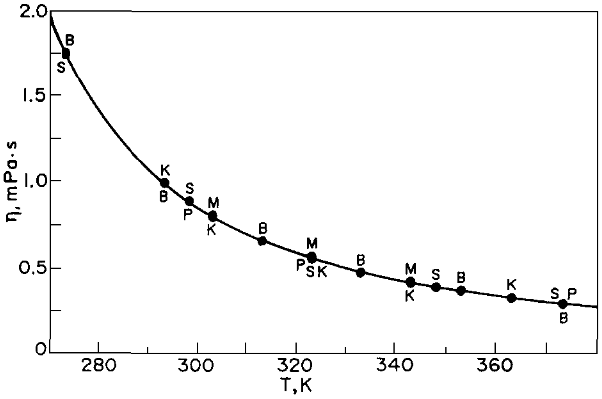

Fig. 3. Viscosity η of water versus temperature at $P=20$ MPa. B, Ref. 21; K, Ref. 15; P, Ref. 17; S, Ref. 18; M, present paper. (——) $\eta=(a+bT+cT^2)^{-1}$.

determined. Moreover, if the determination of ρ is sufficiently precise, the excess volume V^E, which is characteristic of the intermolecular interactions, can be evaluated. For this reason we also present values of density ρ, measured as a function of pressure, temperature, and composition for the three binary mixtures involved. For water + 2-propanol it is important to mention that, if there are already data concerning variations of η versus P,T and composition (as previously indicated), there are no precise data concerning the variations of ρ, and hence of V^E, versus P,T and composition.

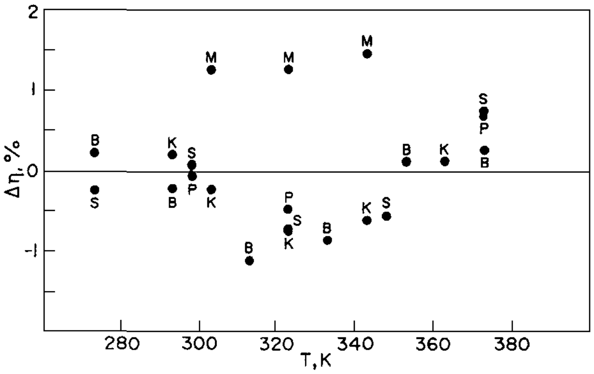

Fig. 4. Deviations $\Delta\eta$ of the literature data for the viscosity of water from the correlation of $\eta=(a+bT+cT^2)^{-1}$ ($P=20$ MPa). B, Ref. 21; K, Ref. 15; P, Ref. 17; S, Ref. 18; M, present paper.

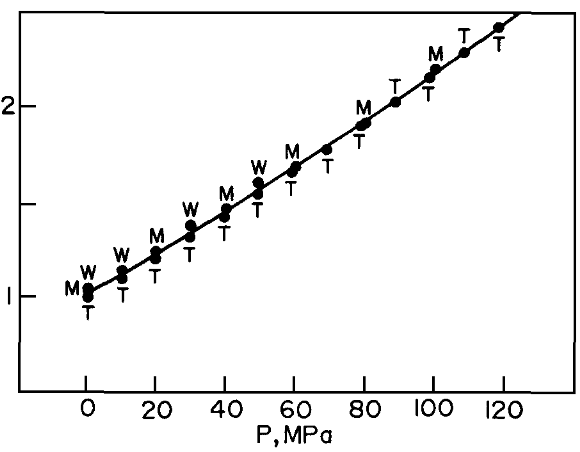

Fig. 5. Viscosity η of 2-propanol versus pressure at $T = 323.15$ K. T, Ref. 9; W, Ref. 22; M, present paper. (——) $\eta = a + bP + cP^2$.

2. EXPERIMENTAL

2.1. Apparatus

The viscosity η is determined with the aid of a falling-body viscometer, technical details of which are provided in Ref. 10. Values of ρ between 0.1 and 70 MPa have been measured with an Anton-Paar DMA 60 + DMA 601 resonance densitometer with an additional 512 P cell. The values are extrapolated to $P = 100$ MPa according to the procedure described in Ref. 10.

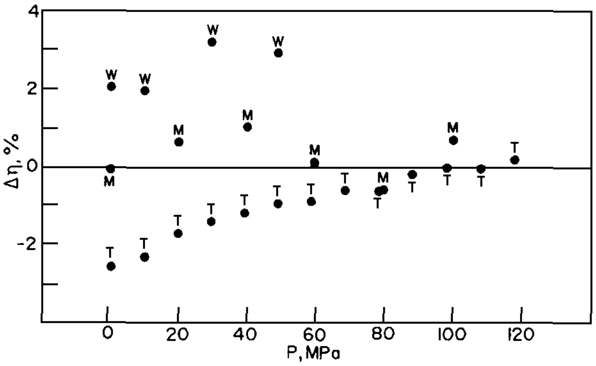

Fig. 6. Deviations $\Delta\eta$ of the literature data for the viscosity of 2-propanol from the correlation of $\eta = a + bP + cP^2$ ($T = 323.15$ K). T, Ref. 9; W, Ref. 22; M, present paper.

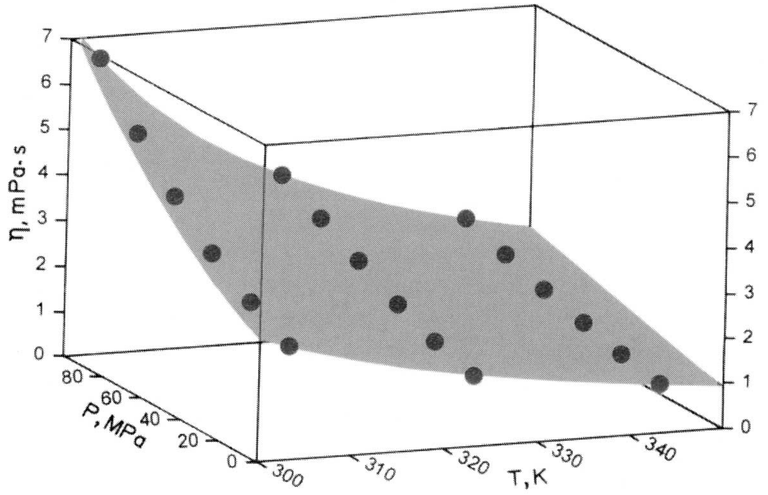

Fig. 7. Viscosity η of DAA versus pressure and temperature.

The uncertainty of the temperature T is estimated as ± 0.5 K for measurements of η, and ± 0.05 K as the uncertainty for ρ. The uncertainty on pressure P is estimated to be ± 0.05 MPa for the measurement of ρ and ± 0.1 MPa for the measurement of η (except at $P = 0.1$ MPa). The uncertainty of ρ is less than 0.1 $kg \cdot m^{-3}$ (except at $P = 0.1$ MPa, where it is

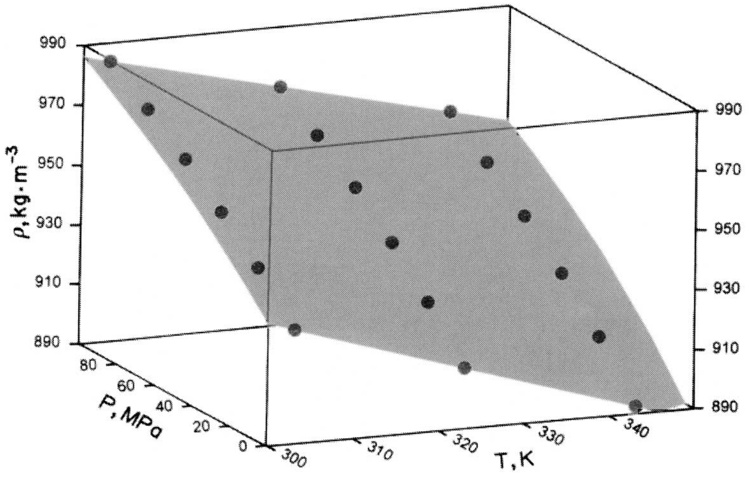

Fig. 8. Density ρ of DAA versus pressure and temperature.

estimated to be below 0.03 $kg \cdot m^{-3}$), which corresponds to the estimate made by Papaioannou et al. [4] with an identical apparatus (with the 512 cell limited to 40 MPa, instead of the more recent 512P cell limited to 70 MPa). The uncertainty of η is of the order of 2%. As discussed previously [10–12], 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. 12, which plots our values and those obtained by other authors. It should be pointed out that, at atmospheric pressure, the kinematics viscosity η/ρ has been determined with a classical capillary viscometer. For this purpose, several KPG tubes, connected to a semiautomatic S/1 Lauda analyser, were used. In this case, during the measurement the uncertainty of the temperature is ±0.01 K.

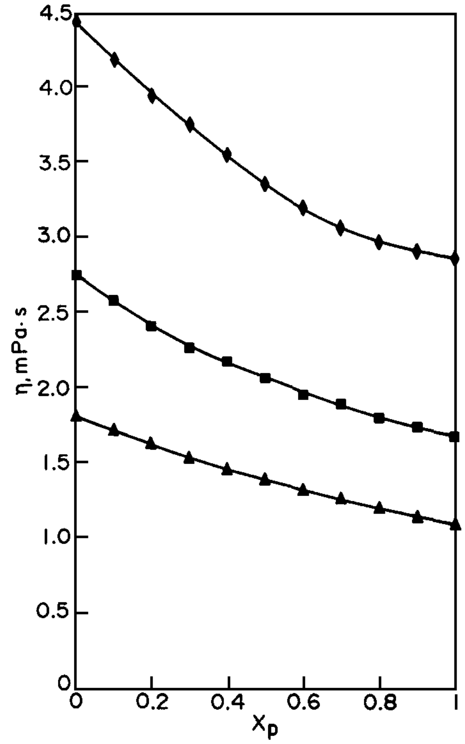

Fig. 9. Viscosity η of the 2-propanol + DAA system at $P = 60$ MPa versus molar fraction x_p of 2-propanol for various temperatures. (◆) 303.15 K; (■) 323.15 K; (▲) 343.15 K.

After multiplying by ρ, the dynamic viscosity η is obtained with an uncertainty of less than 1 %.

2.2. Characteristics of the Samples

The water (H_2O; molar mass $M = 18.015\ g \cdot mol^{-1}$) is distilled water. The two other substances used are commercially available chemicals with the following purity levels: DAA ($C_6H_{12}O_2$; Interchim; purity >99%, molar mass $M = 116.16\ g \cdot mol^{-1}$) and 2-propanol ($C_3H_8O$; Sigma-Aldrich; purity >99.5%, molar mass $M = 60.1\ g \cdot mol^{-1}$). The mixtures were prepared by weighing at atmospheric pressure and ambient temperature so to obtain molar fractions $x_i = 0.1$, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8,

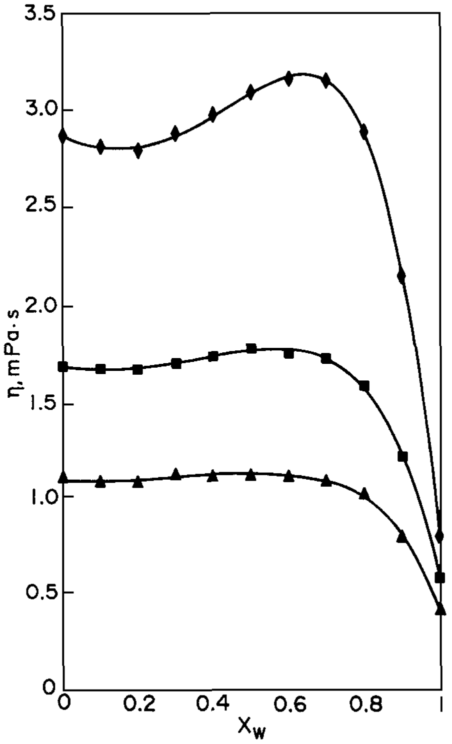

Fig. 10. Viscosity η of the water + 2-propanol system at $P = 60$ MPa versus mole fraction x_w of water for various temperatures. (◆) 303.15 K; (■) 323.15 K; (▲) 343.15 K.

and 0.9. The samples were studied immediately after their preparation to prevent water 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 η and ρ were taken at 303.15, 323.15, and 343.15 K. Measurements of viscosity η were made at 0.1, 20, 40, 60, 80, and 100 MPa. A total of 540 experimental points was obtained for η: 54 for the three pure substances and 486 for the three binary mixtures ($x_i \neq 0$ and

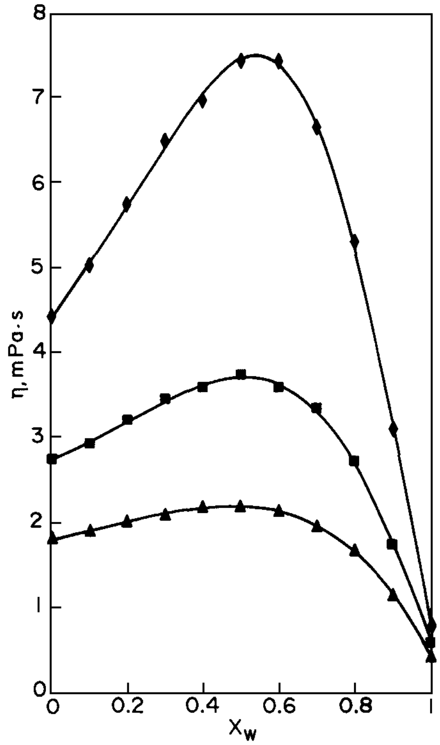

Fig. 11. Viscosity η of the water + DAA system at $P = 60$ MPa versus mole fraction x_w of water for various temperatures. (◆) 303.15 K; (■) 323.15 K; (▲) 343.15 K.

$x_i \neq 1$). Measurements of the density ρ were carried out at pressures from atmospheric pressure, 0.1 MPa, to 65 MPa in progressive 5-MPa steps. There are 1260 experimental values for ρ: 126 for the three pure substances and 1134 for the three binary mixtures ($x_i \neq 0$ and $x_i \neq 1$). Moreover, values of ρ extrapolated to 80 and 100 MPa with the aid of a Tait-type relationship [10] are also indicated. However, to reduce the length of the tabulated data, we retain only those temperatures and pressures for which viscosity has been measured. Additional density (900 values) are available upon request and will also be published soon in Ref. 13. Table I presents, for each pure fluid, the values measured as a function of P and T. Tables II–IV present, for each binary mixture, the values measured as a function of P, T and composition expressed as a mole fraction.

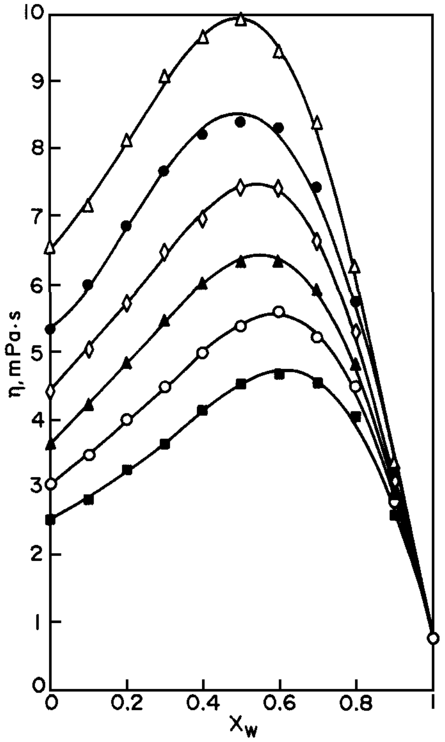

Fig. 12. Viscosity η of the water + DAA system, at $T = 303.15$ K, versus mole fraction x_w of water for various pressures. (■) 0.1 MPa; (○) 20 MPa; (▲) 40 MPa; (◇) 60 MPa; (●) 80 MPa; (△) 100 MPa.

Table I. Viscosity η and Density ρ of Water, 2-Propanol, and DAA, Versus Temperature T and Pressure P

		Water		2-Propanol		DAA	
P (MPa)	T (K)	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)
0.1	303.15	995.6	798	776.4	1750	929.1	2510
20	303.15	1004.3	808	793.0	2070	942.6	3030
40	303.15	1012.7	812	806.7	2410	954.5	3650
60	303.15	1020.8	802	818.4	2860	965.0	4430
80	303.15	1028.5	798	828.6	3240	974.5	5340
100	303.15	1036.0	808	837.8	3700	983.2	6530
0.1	323.15	988.0	547	758.3	1020	910.8	1570
20	323.15	996.5	562	776.9	1240	925.7	1870
40	323.15	1004.7	571	792.0	1470	938.7	2260
60	323.15	1012.6	587	804.9	1690	950.1	2740
80	323.15	1020.1	587	815.9	1920	960.2	3190
100	323.15	1027.4	602	825.8	2200	969.4	3690
0.1	343.15	977.8	404	738.6	650	892.4	1070
20	343.15	986.3	418	760.1	770	909.1	1290
40	343.15	994.6	423	776.7	927	923.1	1550
60	343.15	1002.5	427	790.7	1100	935.3	1800
80	343.15	1010.0	442	802.6	1240	946.1	2110
100	343.15	1017.3	442	813.1	1390	955.9	2440

Table II. Viscosity η and Density ρ of Water + DAA Versus Temperature T, Pressure P, and Mole Fraction x_w of Water

		303.15 K		323.15 K		343.15 K	
P (MPa)	x_w	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)
0.1	0.1	933.7	2810	915.4	1690	896.7	1100
20	0.1	946.9	3480	929.9	2080	913.0	1370
40	0.1	958.5	4220	942.4	2490	926.8	1620
60	0.1	968.8	5040	953.8	2920	938.9	1910
80	0.1	978.1	6000	963.9	3430	949.6	2230
100	0.1	986.7	7130	973.1	4020	959.2	2570
0.1	0.2	938.1	3270	919.8	1820	901.2	1190
20	0.2	950.9	4020	933.9	2270	917.1	1450
40	0.2	962.1	4840	946.3	2700	930.4	1710
60	0.2	972.2	5750	957.1	3200	942.3	2000
80	0.2	981.3	6860	966.9	3760	952.7	2330
100	0.2	989.6	8120	975.7	4430	962.2	2710

Table II. (*Continued*)

		303.15 K		323.15 K		343.15 K	
P (MPa)	x_w	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)
0.1	0.3	943.4	3650	925.2	2060	906.5	1250
20	0.3	955.8	4510	938.9	2510	921.9	1530
40	0.3	966.7	5480	950.9	2930	934.9	1800
60	0.3	976.5	6490	961.5	3460	946.5	2090
80	0.3	985.3	7680	971.1	3940	956.6	2420
100	0.3	993.4	9070	979.8	4610	965.7	2780
0.1	0.4	949.4	4150	930.9	2100	912.2	1290
20	0.4	961.3	5000	944.0	2610	926.9	1620
40	0.4	971.9	6040	955.6	3070	939.4	1910
60	0.4	981.4	6980	966.0	3600	950.7	2200
80	0.4	990.1	8230	975.3	4120	960.5	2510
100	0.4	998.0	9650	983.8	4720	969.5	2760
0.1	0.5	956.2	4550	937.8	2300	919.0	1410
20	0.5	967.4	5400	950.2	2800	933.1	1680
40	0.5	977.7	6370	961.3	3260	945.1	1910
60	0.5	986.8	7440	971.4	3760	955.9	2190
80	0.5	995.2	8420	980.4	4220	965.5	2490
100	0.5	1002.9	9910	988.8	4820	974.3	2820
0.1	0.6	963.4	4710	945.3	2320	926.5	1380
20	0.6	974.2	5620	957.0	2800	939.6	1660
40	0.6	983.9	6350	967.7	3180	951.2	1890
60	0.6	992.6	7450	977.3	3600	961.6	2140
80	0.6	1000.6	8320	986.0	4090	971.0	2370
100	0.6	1008.0	9430	994.1	4490	979.6	2620
0.1	0.7	972.5	4570	954.7	2310	936.4	1370
20	0.7	982.6	5240	965.8	2700	948.7	1590
40	0.7	991.9	5960	975.8	2990	959.5	1770
60	0.7	1000.2	6670	984.8	3350	969.2	1960
80	0.7	1007.9	7440	996.6	3710	978.1	2170
100	0.7	1014.9	8410	1007.7	4080	986.2	2370
0.1	0.8	982.7	4080	965.7	2090	947.9	1240
20	0.8	992.0	4530	975.9	2340	959.2	1410
40	0.8	1000.6	4850	985.0	2540	969.0	1540
60	0.8	1008.5	5330	993.5	2730	978.2	1680
80	0.8	1015.9	5780	1004.2	2990	986.5	1800
100	0.8	1022.8	6280	1014.4	3230	994.2	1950
0.1	0.9	993.3	2600	979.1	1480	963.2	959
20	0.9	1002.2	2800	988.0	1610	972.9	1030
40	0.9	1010.0	2930	996.3	1670	981.7	1100
60	0.9	1017.3	3120	1004.1	1750	990.1	1150
80	0.9	1024.0	3240	1013.5	1820	997.9	1210
100	0.9	1030.3	3360	1022.5	1900	1005.2	1300

Table III. Viscosity η and Density ρ of Water + 2-Propanol Versus Temperature T, Pressure P, and Mole Fraction x_w of Water

		303.15 K		323.15 K		343.15 K	
P (MPa)	x_w	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)
0.1	0.1	785.6	1770	766.9	1030	746.7	648
20	0.1	801.6	2070	785.1	1250	767.6	779
40	0.1	815.0	2430	799.8	1440	784.0	921
60	0.1	826.5	2810	812.3	1680	797.6	1080
80	0.1	836.6	3210	823.2	1880	809.2	1230
100	0.1	845.6	3650	832.8	2110	819.4	1400
0.1	0.2	794.9	1830	776.0	1080	755.7	655
20	0.2	810.4	2100	793.5	1260	775.9	794
40	0.2	823.5	2480	807.8	1450	791.8	924
60	0.2	834.7	2790	820.1	1670	805.1	1070
80	0.2	844.6	3200	830.8	1880	816.5	1210
100	0.2	853.4	3640	840.3	2140	826.6	1350
0.1	0.3	805.9	1950	787.0	1110	766.8	693
20	0.3	820.9	2220	803.8	1310	786.1	842
40	0.3	833.5	2550	817.7	1510	801.5	949
60	0.3	844.3	2890	829.6	1710	814.5	1120
80	0.3	854.0	3270	839.9	1920	825.6	1260
100	0.3	862.6	3670	849.1	2150	835.5	1390
0.1	0.4	818.6	2100	799.9	1210	779.9	731
20	0.4	832.9	2350	815.9	1380	798.1	854
40	0.4	845.0	2670	829.2	1560	812.7	982
60	0.4	855.6	2980	840.7	1740	825.4	1100
80	0.4	864.9	3340	850.9	1940	836.3	1230
100	0.4	873.2	3750	860.1	2160	846.0	1350
0.1	0.5	833.9	2250	815.5	1260	795.8	775
20	0.5	847.4	2490	830.4	1430	812.8	881
40	0.5	858.9	2780	843.1	1610	826.7	1010
60	0.5	869.1	3100	854.1	1790	838.7	1120
80	0.5	878.2	3460	864.1	1960	849.3	1260
100	0.5	886.4	3870	873.0	2140	858.9	1400
0.1	0.6	852.6	2420	834.6	1370	815.4	826
20	0.6	865.2	2650	848.5	1480	831.1	917
40	0.6	876.2	2910	860.5	1640	844.1	1020
60	0.6	885.9	3170	871.0	1760	855.6	1110
80	0.6	894.7	3520	880.3	1930	865.6	1210
100	0.6	902.6	3840	888.8	2130	874.6	1320
0.1	0.7	877.4	2540	859.5	1370	841.0	871
20	0.7	888.8	2700	872.1	1490	855.0	932
40	0.7	898.9	2940	883.2	1600	867.0	1010
60	0.7	908.1	3170	893.0	1730	877.7	1090
80	0.7	916.4	3430	901.9	1840	887.2	1170
100	0.7	924.1	3710	910.1	1960	895.9	1280

Table III. (*Continued*)

		303.15 K		323.15 K		343.15 K	
P (MPa)	x_w	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)
0.1	0.8	909.5	2470	892.7	1370	875.0	846
20	0.8	919.6	2610	903.8	1440	887.4	896
40	0.8	928.8	2770	913.7	1500	897.9	942
60	0.8	937.2	2900	922.6	1600	907.5	1020
80	0.8	944.9	3070	934.2	1690	916.1	1070
100	0.8	952.1	3290	945.2	1790	923.9	1100
0.1	0.9	950.7	1950	936.1	1140	920.6	713
20	0.9	959.1	2010	945.2	1150	930.5	739
40	0.9	967.0	2100	953.6	1190	939.5	768
60	0.9	974.4	2170	961.4	1230	948.0	802
80	0.9	981.3	2220	971.2	1260	955.8	830
100	0.9	987.8	2320	980.4	1330	963.2	870

Table IV. Viscosity η and Density ρ of 2-Propanol + DAA Versus Temperature T, Pressure P, and Mole Fraction x_p of 2-Propanol

		303.15 K		323.15 K		343.15 K	
P (MPa)	x_p	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)
0.1	0.1	919.9	2390	901.5	1500	883.0	1020
20	0.1	933.6	2900	916.6	1800	899.8	1230
40	0.1	945.6	3470	929.5	2160	914.0	1470
60	0.1	956.2	4180	941.1	2570	926.3	1720
80	0.1	965.5	5010	951.2	3010	937.2	2010
100	0.1	974.2	6070	960.5	3510	947.0	2320
0.1	0.2	909.7	2290	891.3	1430	872.5	973
20	0.2	923.5	2720	906.5	1710	889.7	1160
40	0.2	935.6	3290	919.7	2040	904.0	1390
60	0.2	946.2	3940	931.3	2410	916.4	1630
80	0.2	955.6	4700	941.4	2810	927.3	1900
100	0.2	964.4	5710	950.8	3300	937.2	2190
0.1	0.3	898.6	2190	879.9	1360	860.9	923
20	0.3	912.5	2590	895.5	1630	878.5	1110
40	0.3	924.7	3160	908.8	1940	893.1	1320
60	0.3	935.5	3750	920.5	2270	905.7	1540
80	0.3	945.0	4430	930.9	2650	916.6	1790
100	0.3	953.8	5290	940.4	3110	926.4	2050

Table IV. (*Continued*)

		303.15 K		323.15 K		343.15 K	
P (MPa)	x_p	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)	ρ (kg·m^{-3})	η (μPa·s)
0.1	0.4	886.0	2090	867.5	1290	848.4	875
20	0.4	900.4	2490	883.4	1560	866.3	1050
40	0.4	912.6	3010	896.9	1860	881.1	1250
60	0.4	923.6	3550	908.7	2180	893.8	1460
80	0.4	933.2	4170	919.1	2540	904.8	1690
100	0.4	942.0	4930	928.6	2970	914.7	1930
0.1	0.5	872.7	2000	853.9	1230	834.7	828
20	0.5	887.1	2370	870.0	1490	852.9	1000
40	0.5	899.6	2860	883.8	1760	867.9	1190
60	0.5	910.6	3350	895.7	2070	880.9	1390
80	0.5	920.4	3960	906.2	2400	892.2	1610
100	0.5	929.4	4610	915.7	2790	902.4	1830
0.1	0.6	857.7	1910	838.9	1180	819.5	785
20	0.6	872.3	2280	855.3	1430	838.2	957
40	0.6	885.0	2740	869.3	1680	853.5	1120
60	0.6	896.1	3200	881.4	1960	866.5	1330
80	0.6	906.2	3760	892.3	2270	878.2	1520
100	0.6	915.2	4370	902.0	2630	888.4	1730
0.1	0.7	840.7	1840	822.1	1120	802.5	743
20	0.7	855.8	2200	839.0	1380	821.9	910
40	0.7	868.7	2630	853.3	1620	837.4	1090
60	0.7	879.9	3060	865.5	1900	850.7	1270
80	0.7	890.2	3580	876.4	2190	862.3	1460
100	0.7	899.2	4130	886.0	2510	872.5	1650
0.1	0.8	821.9	1780	803.4	1080	783.7	706
20	0.8	837.4	2140	820.7	1310	803.6	864
40	0.8	850.5	2540	835.3	1540	819.5	1030
60	0.8	861.9	2970	847.7	1810	833.1	1200
80	0.8	872.3	3430	858.8	2080	845.0	1370
100	0.8	881.4	3940	868.6	2390	855.3	1550
0.1	0.9	800.7	1750	782.2	1040	762.6	673
20	0.9	816.7	2110	800.2	1260	783.2	811
40	0.9	830.2	2470	815.0	1490	799.4	973
60	0.9	841.7	2910	827.6	1740	813.2	1140
80	0.9	851.6	3320	838.5	2000	824.7	1300
100	0.9	860.7	3800	848.3	2260	834.9	1460

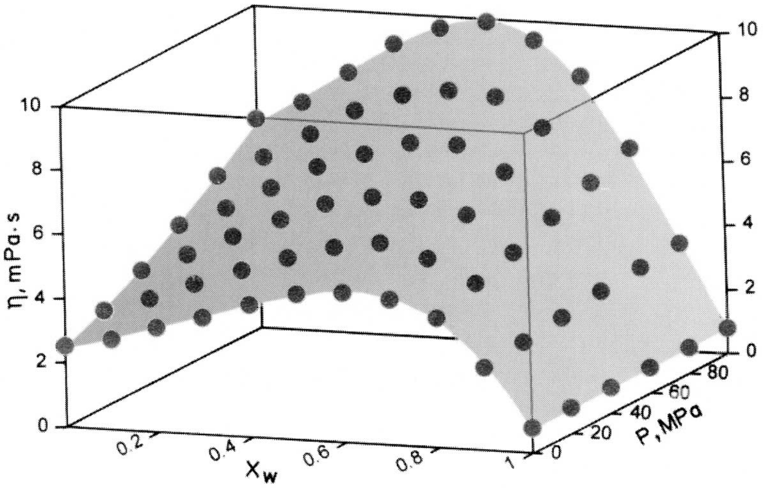

Fig. 13. Viscosity η of the water + DAA system, at $T = 303.15$ K, versus pressure and mole fraction x_w of water.

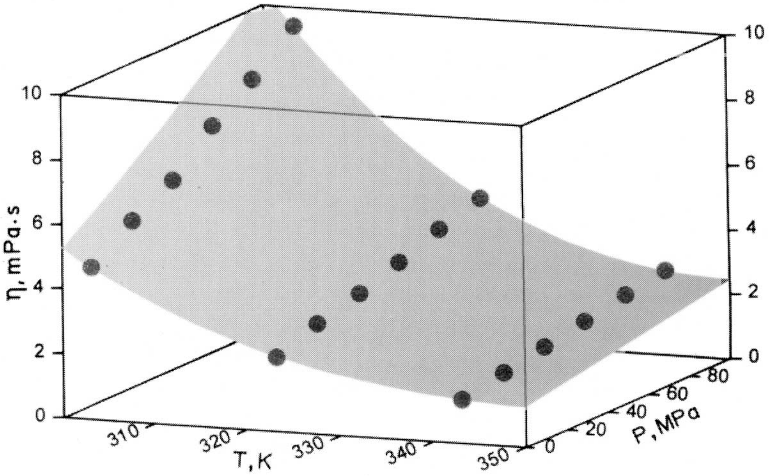

Fig. 14. Viscosity η of the water + DAA system at a mole fraction of water $x_w = 0.6$ versus pressure and temperature.

3.1. Dynamic Viscosity and Density of Pure Substances

For pure water one can refer to previous publications (see, e.g., Refs. 7 and 14–21). The behavior of the dynamic viscosity of pure water with pressure is very particular since, depending on the temperature T, either the curve representing $\eta(P)$ is monotonic and rising (for T higher than approximately 303.15 K), or it presents a minimum (for T lower than approximately 303.15 K). Between 0.1 and 100 MPa the dynamic viscosity η is practically constant at 303.15 K. At fixed pressure P, the viscosity $\eta(T)$ of water falls when the temperature rises. Figure 1 shows variations of the viscosity $\eta(P)$ of water at 303.15 K with pressure. The data are represented by the equation $\eta(P) = a + bP + cP^2$. Figure 2 shows values of the deviation $\Delta\eta = 100(1 - \eta_{\mathrm{cal}}/\eta_{\mathrm{exp}})$ for data obtained by various authors. Figure 3

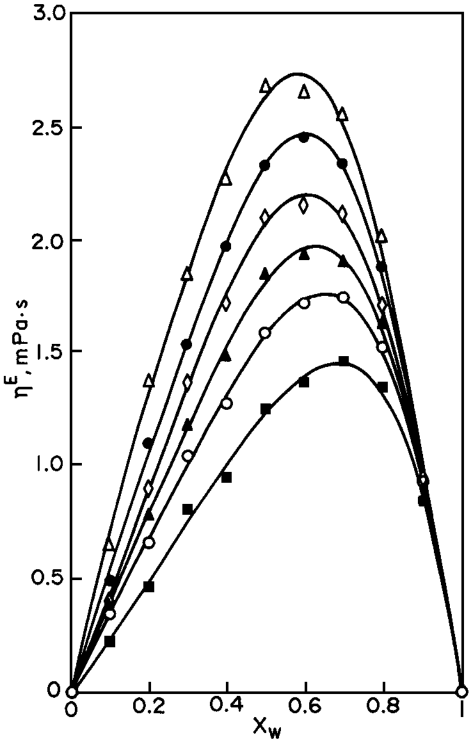

Fig. 15. Excess viscosity η^E of the water + DAA system, at $T = 323.15$ K, versus mole fraction of water x_w, for various pressures. (■) 0.1 MPa; (○) 20 MPa; (▲) 40 MPa; (◇) 60 MPa; (●) 80 MPa; (△) 100 MPa.

shows variations of the viscosity $\eta(T)$ at $P=20$ MPa and Fig. 4 shows variations of $\Delta\eta$ calculated by means of $\eta(T)=(a+bT+cT^2)^{-1}$. The viscosities of 2-propanol and DAA increase with P and decrease with T. For pure 2-propanol one can refer to previous publications (see, e.g., Refs. 9 and 22). A comparison is possible at $T=323.15$ K. Figure 5 shows variations of the viscosity $\eta(P)$ of 2-propanol at $T=323.15$ K with pressure. The data are still represented by the equation $\eta(P)=a+bP+cP^2$. Figure 6 shows values of $\Delta\eta$ for data obtained by various authors. In all cases, for water and 2-propanol, when comparison is possible, there is a good fit between our measurements and those in the literature, to within experimental error. For the three pure substances within the pressure and temperature domain considered, the density increases with P and decreases

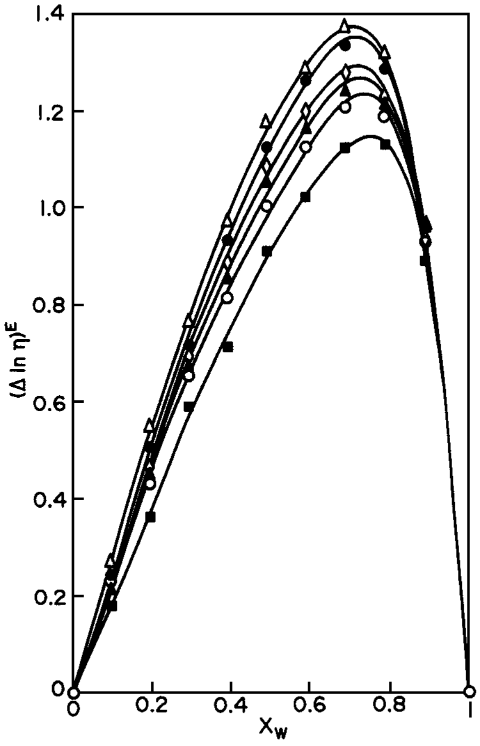

Fig. 16. $(\Delta \ln \eta)^E$ of the water + DAA system, at $T=323.15$ K, versus mole fraction of water x_w, for various pressures. (■) 0.1 MPa; (○) 20 MPa; (▲) 40 MPa; (◇) 60 MPa; (●) 80 MPa; (△) 100 MPa.

with T. Figure 7 represents the surface $\eta(P, T)$ in the case of DAA and Fig. 8 corresponds to the $\rho(P, T)$ for the same substance.

3.2. Viscosity of Binary Mixtures

Figures 9–11 show the viscosity η versus composition, at $P = 60$ MPa, for the three temperatures and the three binaries. The two mixtures containing water exhibit nonmonotonic variation of the viscosity. The deformation of the curves when the temperature varies and the fact that the maximum becomes increasingly marked as the temperature falls can be observed. It is also noted that the maximum is much more clearly marked for water + DAA than for water + 2-propanol. For water + 2-propanol the shape of the $\eta(x_w)$ curve at atmospheric pressure is identical to that already indicated in the literature [8] for this system. The same curve shape (minimum and then maximum in the case of Fig. 10) can be seen for the

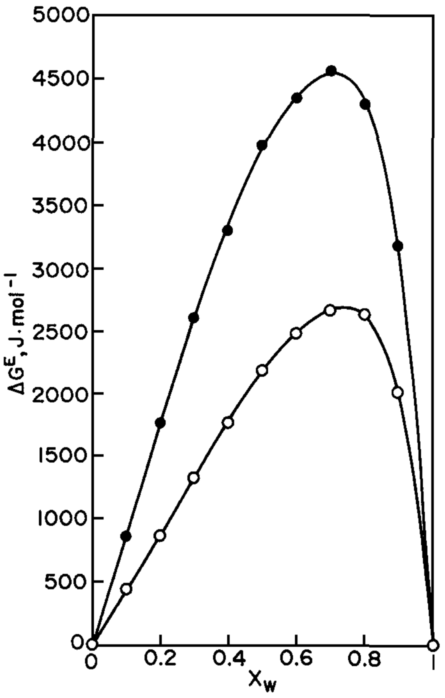

Fig. 17. Excess activation energy of flow ΔG^E versus mole fraction of water x_w, for the water + DAA system (●) and water + 2-propanol system (○), at $P = 60$ MPa and $T = 323.15$ K.

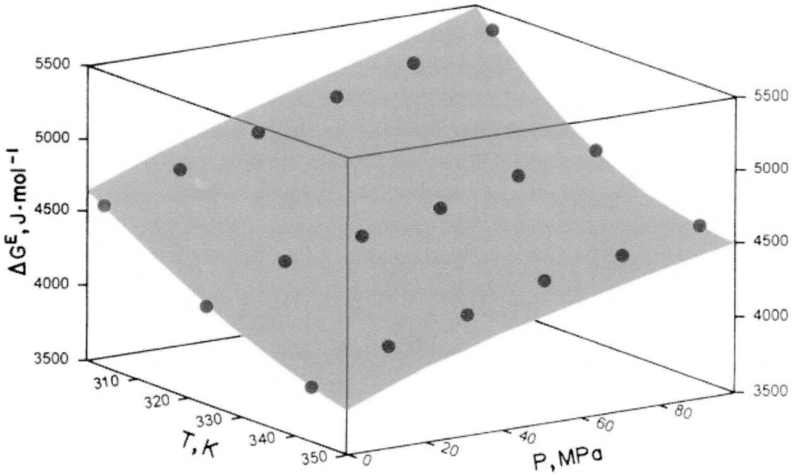

Fig. 18. Excess activation energy of flow ΔG^{E} versus pressure P and temperature T, at $x_{\mathrm{w}} = 0.7$, for the water + DAA system.

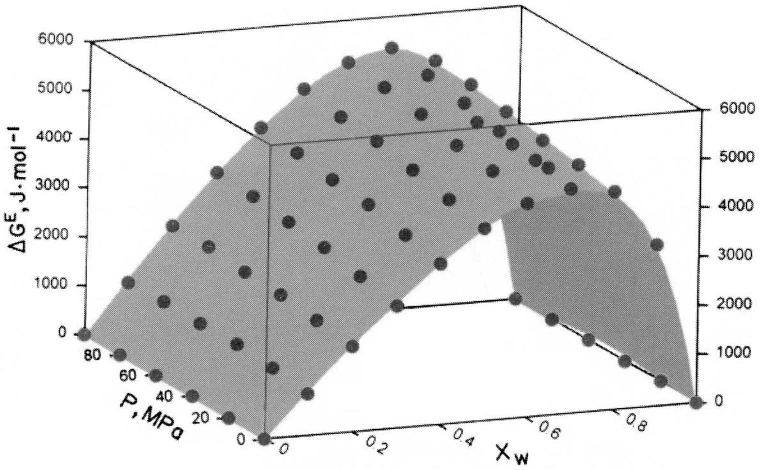

Fig. 19. Variations of excess activation energy of flow ΔG^{E} versus mole fraction of water x_{w} and pressure P, at $T = 323.15$ K, for the water + DAA system.

water + fluoralcohol systems, studied as a function of temperature and pressure [23]. Figure 12 shows the $\eta(x_w)$ curves at $T = 303.15$ K for different pressures (water + DAA). The maximum is all the more marked as the pressure is high and the maximum moves in the direction of increasing x_w when the pressure decreases. Figure 13 is the associated surface $\eta(x_w, P)$ at $T = 303.15$ K for the water + DAA system. Finally, Fig. 14 shows the surface $\eta(P, T)$ obtained at $x_w = 0.6$ in the case of the water + DAA system. The behavior is normal in the sense that η increases with pressure P and decreases with temperature T.

An excess viscosity η^E is often introduced; there are several definitions of this parameter. We first chose $\eta^E = \eta - x_1\eta_1 - x_2\eta_2$ (see, e.g., Refs. 24–27). Figure 15 shows variations of the excess viscosity η^E as a function

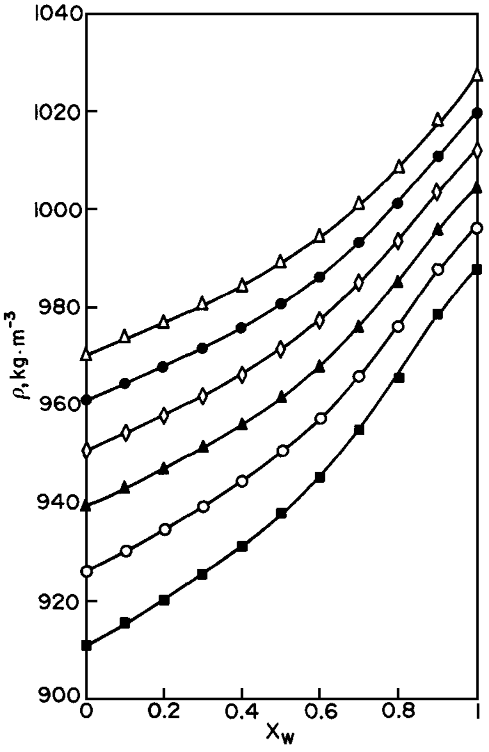

Fig. 20. Density ρ of the water + DAA system at $T = 323.15$ K, versus mole fraction of water x_w, for various pressures. (■) 0.1 MPa; (○) 20 MPa; (▲) 40 MPa; (◇) 60 MPa; (●) 80 MPa; (△) 100 MPa.

of x_w, at $T = 323.15$ K, for various pressures, in the case of water + DAA. It can easily be verified from the experimental data that at a constant x_w, η^E decreases with T and increases with P. For water + DAA it can be verified that $\eta^E > 0$ in all cases. This is also true of water + 2-propanol, for which the curves are similar to those for water + DAA. On the other hand, for 2-propanol + DAA it can be verified that $\eta^E < 0$ in all cases. For this system $|\eta^E|$ increases with P and decreases with T. Moreover, while the effect is very distinctly marked for water + DAA, it is less so for water + 2-propanol and is only slight for 2-propanol + DAA (which seems the least associative). We also considered the relationship $\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2)$, which is sometimes used [6, 28, 29]. The results are qualitatively the same, but of course the value of η^E is not the same. It seems that η^E is greater in the second case than in the first, whether η^E is positive or

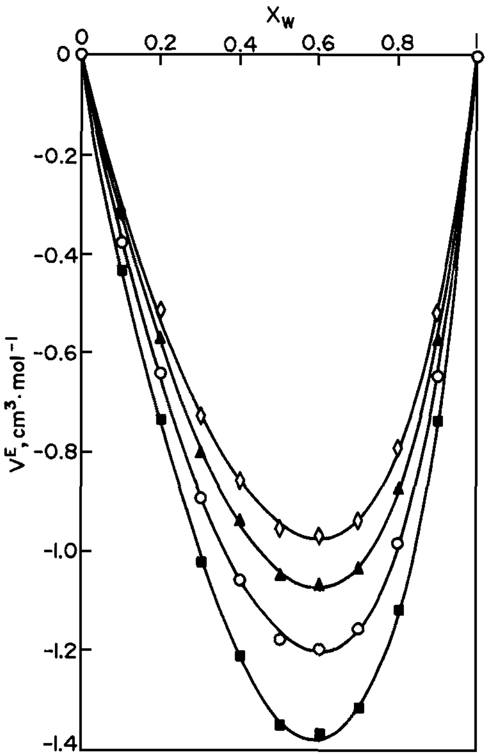

Fig. 21. Excess volume V^E of the water + DAA system at $T = 323.15$ K versus mole fraction of water x_w, for various pressures. (■) 0.1 MPa; (○) 20 MPa; (▲) 40 MPa; (◇) 60 MPa.

negative. Finally, the quantity $(\Delta \ln \eta)^E = \ln \eta - x_1 \ln \eta_1 - x_2 \ln \eta_2$ is sometimes calculated [30–32]. Here, too, the shape of the curve is qualitatively the same. Figure 16 shows variations of $(\Delta \ln \eta)^E$ as a function of the mole fraction of water x_w, at $T = 323.15$ K, for various pressures, in the case of water + DAA. On the basis of the tables it can be verified that $(\Delta \ln \eta)^E$ varies as η^E as a function of pressure, temperature, and composition. However, comparing Figs. 15 and 16, we note that at a given value of pressure, the maximum is not located at the same value of the mole fraction of water. This is probably due to the fact these expressions of η^E and $(\Delta \ln \eta)^E$ do not have a theoretical background. Hence the significance of the maximum presented by the curves needs to be clarified. A similar but more comprehensive study was conducted previously [33], although the authors did not consider the pressure dependence of mixture viscosity. It is

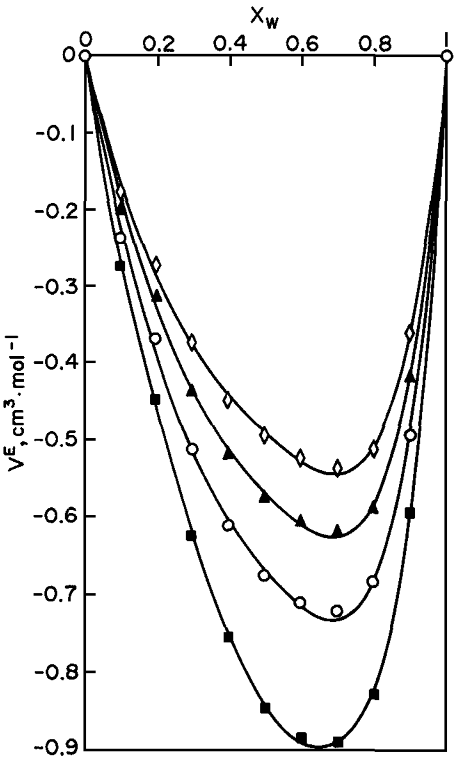

Fig. 22. Excess volume V^E of the water + 2-propanol system at $T = 323.15$ K, versus mole fraction of water x_w, for various pressures. (■) 0.1 MPa; (○) 20 MPa; (▲) 40 MPa; (◇) 60 MPa.

more interesting to calculate, from the η values, the excess activation energy of viscous flow ΔG^E defined by

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + \Delta G^E/(RT) \qquad (1)$$

where $V_i = M_i/\rho_i$ is the molar volume of component i (molecular weight $\sum x_i \cdot M_i$ for the mixture) and R the constant of the perfect gases. This relation is a modified form of Katti and Chaudri's equation [34] and is theoretically justified from Eyring's representation of the dynamic viscosity of a pure fluid [35]. It is interesting to note here that the quantity ηV is also obtained from the time-correlation expression for shear viscosity [36]. Thus the quantities ηV and ΔG^E have a theoretical background, while the η^E expressions do not. The calculation of ΔG^E from the tables is easy. Figure 17 shows the variations of ΔG^E versus x_w for water + DAA and water + 2-propanol, at $P = 60$ MPa and $T = 323.15$ K. The maximum value

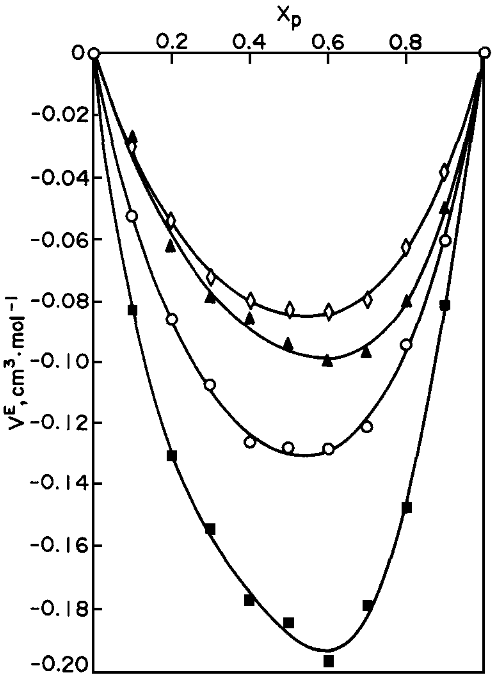

Fig. 23. Excess volume V^E of the 2-propanol + DAA system at $T = 323.15$ K, versus mole fraction of 2-propanol x_p, for various pressures. (■) 0.1 MPa; (○) 20 MPa; (▲) 40 MPa; (◇) 60 MPa.

of ΔG^E is very large for both systems, which are very associative. One can note here that for binary DAA + 2-propanol, ΔG^E is close to zero. Its values are between +120 and −120 $J \cdot mol^{-1}$, i.e., nosignificant (as the uncertainty on viscosity is 2%, then the uncertainty on ΔG^E is about ±100 $J \cdot mol^{-1}$). The values determined show that ΔG^E increases with P and decreases when T increases. Figure 18 shows variations of ΔG^E versus P and T, at $x_w = 0.7$, for the water + DAA system. Figure 19 shows variations of ΔG^E versus P and x_w, at 303.15 K, for the same binary.

3.3. Density of Binary Mixtures and Excess Volume

Regarding the density ρ, its behavior is usual for the three binaries: ρ is observed to decrease with T, increase with P, and vary monotonically

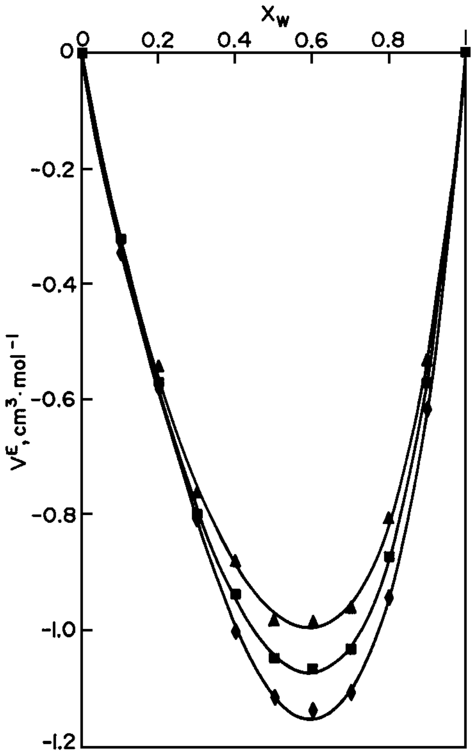

Fig. 24. Excess volume V^E of the water + DAA system at $P = 40$ MPa, versus mole fraction of water x_w, for various temperatures. (◆) 303.15 K; (■) 323.15 K; (▲) 343.15 K.

with the composition x_i. Figure 20 shows variations of ρ as a function of the mole fraction of water x_w at $T = 323.15$ K for different pressures P, in the case of water + DAA. The excess volume V^E can be calculated from our measurements through the relation $V^E = x_1 M_1(\rho^{-1} - \rho_1^{-1}) + x_2 M_2(\rho^{-1} - \rho_2^{-1})$. The apparatus used is sufficiently accurate to provide a satisfactory estimate of V^E. Figures 21–23 represent variations of the excess volume V^E for each of the binaries, as a function of the composition, at $T = 323.15$ K, for the different pressures. There is a marked effect for the binary water + DAA, a little less marked for the binary water + 2-propanol and only slight for the binary DAA + 2-propanol, which suggests decreasing interactions. It is seen that in all three cases V^E is negative whatever the binary, the temperature, the pressure, and the composition. At fixed composition and temperature $|V^E|$ decreases as the pressure increases. At a given composition and pressure $|V^E|$ decreases when the temperature increases (Fig. 24).

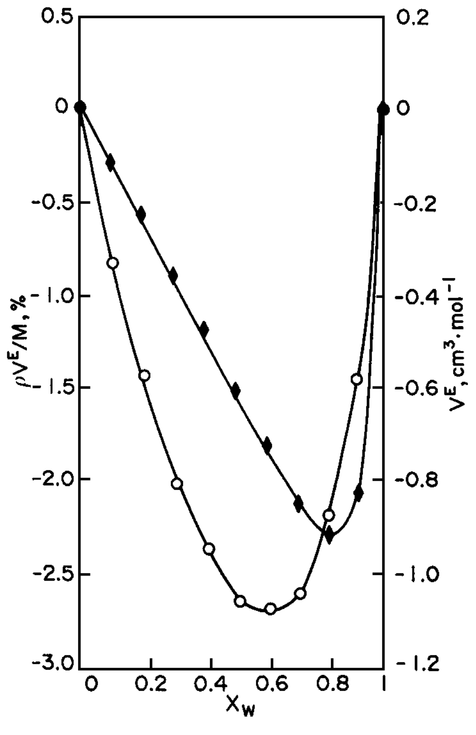

Fig. 25. Excess volume V^E (○) and $\rho V^E/M$ (◆) (%), at $P = 40$ MPa and $T = 323.15$ K, versus mole fraction of water x_w, for the water + DAA system.

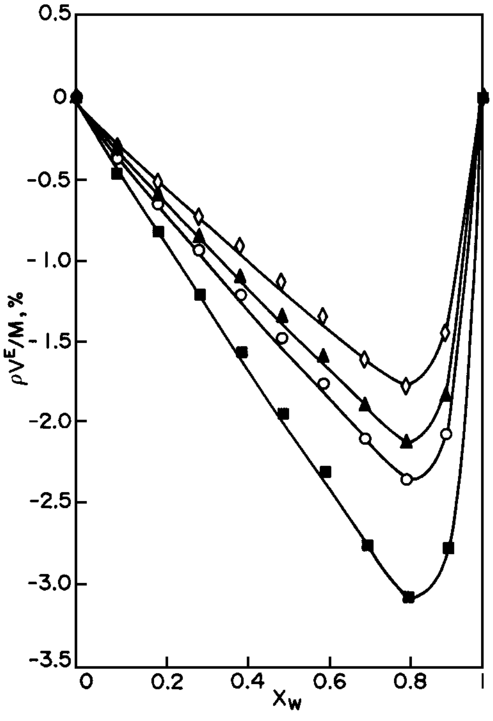

Fig. 26. $\rho V^{E}/M$ (%) versus mole fraction of water at $T=303.15$ K, for the water + 2-propanol system, for various pressures. (■) 0.1 MPa; (○) 40 MPa; (▲) 60 MPa; (◇) 100 MPa.

It should be emphasized here that it is necessary to be careful with regard to the significance of the maximum or minimum of the excess volume V^{E}. This quantity is relative to one mole of the mixture. On the other hand, the quantity $\rho V^{E}/M$ is relative to one unit volume of the mixture. Figure 25 shows the variations of V^{E} and $\rho V^{E}/M$ for the binary water + DAA, at $T=323.15$ K and $P=40$ MPa, versus the mole fraction x_{w} of water. There is a notable discrepancy between the positions of the two minima. For the three binaries the contraction $\rho V^{E}/M$ is maximum at $P=0.1$ MPa and $T=303.15$ K. One obtains -3.06% for water + DAA at $x_{w}=0.8$, -3.08% for water + 2-propanol at $x_{w}=0.8$, and -0.25% for 2-propanol + DAA at $x_{p}=0.6$. It should be noticed that the minimum values of $\rho V^{E}/M$ are almost the same as those for water + DAA and water + 2-propanol but that the minimum value of V^{E} is more marked for the first binary one than for the second. Which one of both quantities is

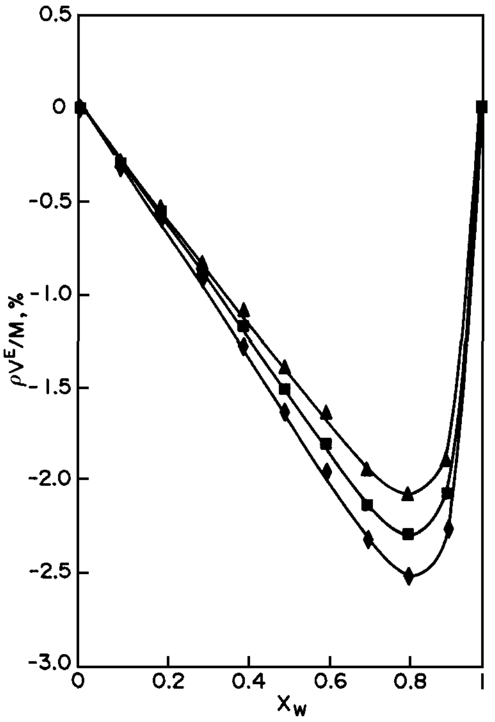

Fig. 27. $\rho V^E/M$ (%) versus mole fraction of water x_w, at $P = 40$ MPa, for the water + DAA system, for various temperatures. (◆) 303.15 K; (■) 323.15 K; (▲) 343.15 K.

really characteristic of the maximum effect of the intermolecular interactions? From the point of view of excess volume (here contraction effect), it seems to us that $\rho V^E/M$ is probably more significant. Figure 26 shows the variations of $\rho V^E/M$ versus mole fraction of water x_w at $T = 303.15$ K for water + 2-propanol at various pressures. Finally, Fig. 27 shows the variations of $\rho V^E/M$ versus mole fraction of water x_w at $P = 40$ MPa for water + DAA and various values of the temperature.

The curves representing η, η^E, $(\Delta \ln \eta)^E$, $(\Delta G)^E$, V^E, and $\rho V^E/M$, as a function of composition, at fixed pressure P and temperature T can be adjusted with a relationship of the Redlich–Kister type. It should be emphasized that there are other relationships able to give an equally satisfactory adjustment. However, the numerical coefficients which appear in those calculations depend not only on the nature of the binary, but also on the P and T values, and this restricts the interest of these empirical relationships, which are above all useful for interpolations. The data supplied in this article could be included in databases and be used later to test more sophisticated models of viscosity η, excess volume V^{E}, and excess activation energy of flow ΔG^{E} with sound theoretical foundations. They allow also some determinations concerning the compressibility coefficient β_T and its excess value β_T^{E}.

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