Density, Viscosity, and Refractive Index of Formamide, Three Carboxylic Acids, and Formamide + Carboxylic Acid Binary Mixtures

Alicia M. Cases, Ana C. Gómez Marigliano, Carlos M. Bonatti, and Horacio N. Sólimo*

Departamento de Física—Facultad de Ciencias Exactas y Tecnología, Universidad Nacional de Tucumán, 4000 Tucumán, Argentina

Density, viscosity, and refractive index measurements of pure formamide and of formic, acetic, and propionic acids in the temperature range (298.15 to 313.15) K were made. Additionally, measurements of the same properties and in the same temperature range were made on the following mixtures: formamide + (formic acid, or + acetic acid, or + propionic acid). The results were fitted to empirical equations, whose calculated values are in agreement with the experimental ones.

Introduction

Experimental data of physical properties such as density, viscosity, and refractive index, at any given temperature for pure components and for binary liquid mixtures in the whole composition range, are useful for a full understanding of the thermodynamic properties of liquids, as well as for practical chemical engineering applications.

The main purposes of this work are (i) to report experimental data on density, viscosity, and refractive index for the following binary mixtures [formamide (F) + (formic acid (FA), or + acetic acid (AA), or + propionic acid (PA))] in the temperature range (298.15 to 313.15) K and in the whole composition range; (ii) to obtain a set of empirical equations for these properties as functions of temperature for the pure components; and (iii) to obtain another set of empirical equations for these properties as functions of temperature and composition for these binary mixtures.

We could not find any information about these binary systems in the available literature.

Experimental Section

Materials. Formamide and propionic acid (Riedel-de Haën, A. R.) were used as received, because their purities were practically 100 mass % (no other chromatographic peak was detected) and >99 mass % (GC), respectively. Acetic acid (Merck, p.a.) was fractionally distilled over anhydrous P_2O_5, collecting only the middle fraction. It had a purity better than 99 mass % (GC). Formic acid (Riedel-de Haën, A. R.) was purified by a fractional-crystallization method based on differences in freezing points of water and acid, to eliminate its main impurity (water). This method was applied several times to reach a purity better than 99 mass % (GC), keeping the acid frozen in order to prevent its decomposition. The purity of all the reagents was determined using a HP 6890 gas chromatograph with a TCD detector coupled with a ChemStation. Nitrogen was used as gas carrier.

Procedure. Mixtures of the desired compositions were prepared by mixing accurately weighed quantities of the pure liquids, using a Mettler Toledo AG245 balance with an appreciation of ±0.1 mg. The reported mole fractions were accurate within ±0.0001. Density, refractive index, and viscosity were measured with a vibrating tube densimeter KEM DA 300 (using degassed bidistilled water and dry air as calibrating substances), a Jena dipping refractometer (calibrated against several glass prisms with well-defined refraction indexes determined by the manufacturer), and Cannon-Fenske viscometers (calibrated with bidistilled water and benzene in order to determine both viscometer constants), respectively. The appreciations were ±0.1 kg m^{-3} for the densimeter and ±0.00002 for the refractometer, while the relative error for the viscosity was $\Delta\eta/\eta = 4 \times 10^{-3}$. In all cases, a thermostatically controlled water bath accurate to ±0.01 K was used. Caution was taken to prevent evaporation.

* Corresponding author. Fax: (54-381) 4363004. E-mail: hsolimo@herrera.unt.edu.ar.

Table 1. Physical Properties of the Pure Chemicals

		ρ/kg m^{-3}		n_D		η/mPa s	
compound	T/K	exp	lit	exp	lit	exp	lit
formamide	298.15	1129.1	1129.15[a]	1.445 97	1.44682[a]	3.23	3.302[a]
	303.15	1124.6		1.444 32		2.83	
	308.15	1120.2		1.442 58		2.59	
	313.15	1116.1		1.440 54		2.36	
formic acid	298.15	1213.8	1214.05[a]	1.369 43	1.36938[a]	1.51	1.607[b]
	303.15	1207.5		1.367 31		1.36	1.443[a]
	308.15	1201.2		1.365 59		1.25	
	313.15	1194.6		1.363 65		1.15	1.219[c]
acetic acid	298.15	1044.0	1043.92[b]	1.370 46	1.3698[a]	1.06	1.056[b]
	303.15	1038.3		1.368 58		0.98	1.024[a]
	308.15	1032.5		1.366 59		0.91	
	313.15	1027.1		1.364 89		0.86	
propionic acid	298.15	990.3	988.08[a]	1.384 79	1.3843[a]	1.03	1.030[b]
	303.15	985.0		1.382 82		0.96	0.974[a]
	308.15	979.5		1.380 76		0.89	
	313.15	974.3		1.378 84		0.84	0.845[c]

[a] From *Organic Solvents*,[1] pp 360, 362, 364, and 654. [b] From *CRC Handbook of Thermophysical and Thermochemical Data*,[2] pp 83 and 409. [c] From *CRC Handbook of Chemistry and Physics*,[3] pp F-43 and F-44.

Results and Discussion

Experimental results for density, refractive index, and viscosity of pure compounds at 298.15, 303.15, 308.15, and 313.15 K are summarized in Table 1, along with those found in the literature for comparison.[1−3]

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Table 2. Experimental Density (ρ), Viscosity (η), and Refractive Index (n_D) at Several Temperatures for Formamide (F) + Carboxylic Acid Binary Systems

	ρ/kg m^{-3}				η/mPa s				n_D			
x_F	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
					(a) [(x)formamide + (1 − x)formic acid]							
0.0000	1213.8	1207.5	1201.2	1194.6	1.51	1.36	1.25	1.15	1.369 43	1.367 31	1.365 59	1.363 65
0.0748	1211.8	1205.7	1199.6	1193.3	1.77	1.58	1.45	1.33	1.377 04	1.375 19	1.373 48	1.371 74
0.1535	1208.3	1202.5	1196.6	1190.5	2.01	1.79	1.65	1.52	1.384 44	1.382 57	1.380 82	1.379 07
0.2286	1203.9	1198.3	1192.5	1186.7	2.25	2.00	1.83	1.68	1.391 07	1.389 24	1.387 45	1.385 91
0.3078	1197.7	1192.2	1186.6	1180.9	2.50	2.21	2.02	1.84	1.397 45	1.395 64	1.393 79	1.392 19
0.3891	1191.3	1186.0	1180.6	1175.1	2.81	2.47	2.26	2.07	1.403 71	1.401 83	1.400 04	1.398 20
0.4554	1185.1	1179.9	1174.6	1169.2	2.86	2.52	2.30	2.10	1.408 67	1.406 82	1.405 06	1.403 34
0.5248	1178.3	1173.2	1168.0	1162.5	2.98	2.62	2.39	2.18	1.413 72	1.411 90	1.410 08	1.408 53
0.6239	1168.0	1163.2	1158.1	1153.0	3.06	2.69	2.46	2.24	1.420 58	1.418 79	1.417 12	1.415 27
0.6923	1161.0	1156.2	1151.3	1146.6	3.09	2.72	2.48	2.25	1.424 74	1.422 70	1.421 04	1.419 30
0.7982	1150.1	1145.4	1140.8	1136.2	3.13	2.74	2.49	2.47	1.432 46	1.430 47	1.428 93	1.427 06
0.8449	1145.2	1140.5	1136.0	1131.5	3.12	2.73	2.48	2.26	1.435 35	1.433 60	1.432 15	1.430 66
0.9202	1137.3	1132.8	1128.3	1123.9	3.11	2.72	2.47	2.25	1.440 47	1.438 52	1.437 05	1.435 32
1.0000	1128.7	1124.6	1120.2	1116.1	3.23	2.84	2.59	2.36	1.445 97	1.444 32	1.442 58	1.440 54
					(b) [(x)formamide + (1 − x)acetic acid]							
0.0000	1044.0	1038.3	1032.5	1027.1	1.06	0.98	0.91	0.86	1.370 46	1.368 58	1.366 59	1.364 89
0.0782	1057.2	1051.6	1046.4	1040.9	1.54	1.39	1.28	1.19	1.378 07	1.376 04	1.374 24	1.372 15
0.1552	1068.2	1062.8	1057.7	1052.4	2.07	1.84	1.68	1.54	1.384 95	1.382 91	1.381 34	1.379 29
0.2319	1077.4	1072.2	1067.0	1062.0	2.63	2.30	2.09	1.89	1.391 24	1.389 29	1.387 64	1.385 91
0.3049	1085.1	1080.0	1075.1	1069.9	3.11	2.71	2.43	2.19	1.396 96	1.395 01	1.393 28	1.391 42
0.3832	1092.5	1087.5	1082.6	1077.6	3.54	3.06	2.73	2.45	1.402 49	1.400 11	1.399 04	1.397 03
0.4595	1098.1	1093.2	1088.4	1083.6	3.85	3.32	2.95	2.65	1.407 83	1.405 75	1.404 27	1.402 51
0.5395	1104.1	1099.2	1094.5	1089.8	4.04	3.52	3.08	2.81	1.413 33	1.411 49	1.409 53	1.407 78
0.6155	1108.9	1104.1	1099.5	1094.9	4.02	3.50	3.10	2.77	1.418 48	1.416 70	1.414 96	1.412 76
0.6939	1113.5	1108.9	1104.4	1099.9	3.97	3.49	3.08	2.75	1.424 15	1.421 76	1.420 07	1.418 21
0.7683	1117.2	1112.6	1108.2	1103.8	3.83	3.40	2.97	2.67	1.428 14	1.427 19	1.424 71	1.423 63
0.8477	1121.3	1116.8	1112.5	1108.6	3.57	3.10	2.79	2.53	1.435 09	1.432 92	1.431 45	1.429 69
0.9228	1125.3	1121.0	1116.7	1112.9	3.36	2.94	2.65	2.40	1.440 05	1.438 24	1.436 86	1.435 18
1.0000	1128.7	1124.6	1120.2	1116.1	3.23	2.84	2.59	2.36	1.445 97	1.444 32	1.442 58	1.440 54
					(c) [(x)formamide + (1 − x)propionic acid]							
0.0000	990.3	985.0	979.5	974.3	1.03	0.96	0.89	0.84	1.384 79	1.382 82	1.380 76	1.378 84
0.0769	1000.6	995.4	990.2	985.0	1.40	1.28	1.19	1.09	1.389 73	1.387 73	1.385 62	1.383 90
0.1507	1011.4	1006.4	1001.2	996.3	1.89	1.70	1.57	1.46	1.394 49	1.392 56	1.390 86	1.388 68
0.2323	1023.2	1018.2	1013.3	1008.3	2.54	2.25	2.05	1.89	1.399 48	1.397 60	1.395 90	1.393 93
0.3109	1033.9	1029.0	1024.2	1019.3	3.21	2.78	2.50	2.27	1.404 56	1.402 72	1.400 96	1.399 54
0.3930	1044.9	1040.1	1035.4	1030.6	3.83	3.28	2.94	2.64	1.409 21	1.407 34	1.405 32	1.403 82
0.4098	1047.1	1042.3	1037.6	1032.8	3.92	3.37	3.01	2.69	1.409 80	1.408 34	1.406 08	1.404 67
0.4649	1054.2	1049.4	1044.7	1040.0	4.24	3.62	3.23	2.89	1.412 91	1.411 34	1.409 11	1.407 64
0.5404	1063.8	1059.1	1054.5	1049.9	4.48	3.83	3.41	3.03	1.417 44	1.415 63	1.413 75	1.412 00
0.6138	1074.2	1069.6	1065.1	1060.5	4.80	4.06	3.60	3.20	1.422 19	1.420 32	1.418 48	1.416 65
0.6916	1084.4	1079.9	1075.4	1070.9	4.70	4.01	3.57	3.18	1.426 64	1.424 74	1.422 92	1.421 09
0.7633	1094.1	1089.7	1085.2	1080.8	4.49	3.84	3.43	3.07	1.430 43	1.429 03	1.427 00	1.425 43
0.8461	1107.8	1103.5	1099.3	1095.0	4.22	3.63	3.26	2.93	1.435 97	1.434 17	1.432 60	1.430 84
0.9226	1119.1	1114.9	1110.6	1106.3	3.75	3.25	2.94	2.66	1.440 45	1.438 82	1.437 11	1.435 32
1.0000	1128.7	1124.6	1120.2	1116.1	3.23	2.83	2.59	2.36	1.445 97	1.444 32	1.442 58	1.440 54

Table 3. Coefficients and Standard Deviations of Eqs 1, 2, and 3

	ρ/kg m^{-3}			n_D			η/mPa s		
compound	a_1	b_1	$\sigma^{a,b}$	a_2	$10^4 b_2$	$10^4\sigma$	$10^3 a_3$	b_3	$\sigma^{a,b}$
formamide	1149.8	−0.84	0.1	1.4551	−3.6	1	5.0	1900	0.2
formic acid	1245.8	−1.28	0.1	1.3789	−3.8	1	5.5	1700	0.1
acetic acid	1072.2	−1.13	0.1	1.3798	−3.7	1	13	1300	0.03
propionic acid	1017.1	−1.07	0.1	1.3947	−4.0	1	13	1280	0.07

[a] $\sigma = [\sum(P_{exp} - P_{calc})^2/N]^{1/2}$, where P represents ρ, η, or n_D, and N is the number of experimental points. [b] Units: ρ/kg m^{-3} and η/mPa s.

The viscosity of all the components does not have a linear behavior with temperature, particularly for formamide, as is expected for associated liquids, while both density and refractive index have linear plots.

Experimental results of density, refractive index, and viscosity at the same temperatures for the systems (F + FA), (F + AA), and (F + PA) in the whole composition range are listed in Table 2.

The following functional relationships for the density, refractive index, and viscosity of the pure compounds with temperature were used.

$$\rho = a_1 + b_1 \times t \quad (1)$$

$$n_D = a_2 + b_2 \times t \quad (2)$$

$$\eta = a_3 \exp(b_3/T) \quad (3)$$

where a_1, b_1, a_2, b_2, a_3, and b_3 are constants, and the temperatures t and T are in degrees Celcius and Kelvin, respectively. Equations 1 and 2 were fitted using least squares with all points equally weighted, and eq 3 was fitted with a nonlinear regression method based on the Levenberg−Marquardt algorithm.[4] This allows us to evaluate both constants of these equations. The appropriate number of significant digits was selected taking into account each coefficient error. These values and their standard deviations are collected in Table 3. An examination of Table 1 shows that the refractive indexes decrease with increasing temperature, as happens in most organic liquids. The same behavior can be observed for the densities[5] and viscosities. The temperature coefficients are

Table 4. Equations for Density, Refractive Index, and Viscosity As a Function of the Temperature and Composition for the F + Carboxylic Acid Binary Systems[a]

system	equations	eq no.	σ^a
formamide	$\rho = (1247 - 60x_F - 41x_F^2) + (-1.26 + 0.41x_F) \times t$	(7)	2
+ formic	$n_D = (1.3786 + 0.103x_F - 0.05x_F^2 + 0.024x_F^3) + (-3.6 \times 10^{-4} + (2 \times 10^{-5})x_F) \times t$	(8)	7×10^{-4}
acid	$\ln \eta = (-5.20 - 0.3x_F) + (1670 + 700x_F - 400x_F^2)/T$	(9)	0.09
formamide	$\rho = (1072.4 + 162x_F - 141x_F^2 + 56x_F^3) + (-1.11 + 0.29x_F) \times t$	(10)	0.6
+ acetic	$n_D = (1.3802 + 0.094x_F - 0.04x_F^2 + 0.02x_F^3) + (-3.8 \times 10^{-4} + (2 \times 10^{-5})x_F) \times t$	(11)	5×10^{-4}
acid	$\ln \eta = (-4.4 - 7.4x_F + 6.54x_F^2) + (1350 + 3400x_F - 2900x_F^2)/T$	(12)	0.2
formamide	$\rho = (1016.5 + 132x_F) + (-1.063 + 0.30x_F - 0.08x_F^2) \times t$	(13)	1
+ propionic	$n_D = (1.3948 + 0.0591x_F) + (-3.8 \times 10^{-4} + (4 \times 10^{-5})x_F) \times t$	(14)	5×10^{-4}
acid	$\ln \eta = (-3.9 - 9.1x_F + 7.6x_F^2) + (1180 + 4100x_F - 3300x_F^2)/T$	(15)	0.2

[a] Units: ρ/kg m^{-3} and η/mPa s.

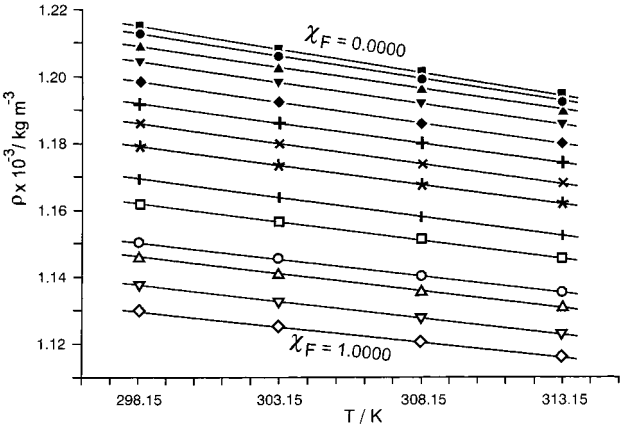

Figure 1. Density versus temperature for the formamide + formic acid binary system in the whole concentration range.

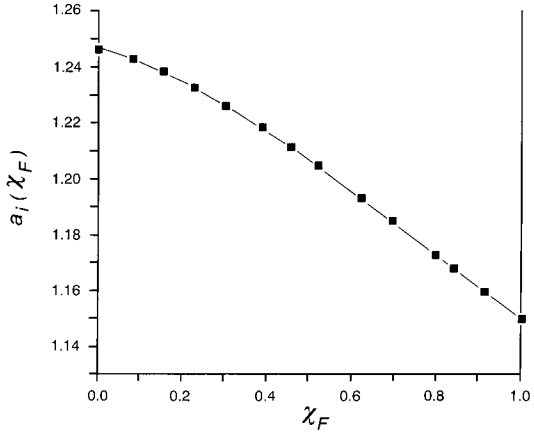

Figure 2. Parameter $a_i(x_F)$ in eq 4 versus mole fraction of formamide.

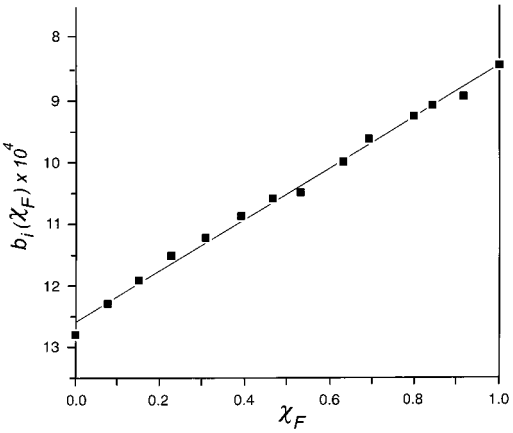

Figure 3. Parameter $b_i(x_F)$ in eq 4 versus mole fraction of formamide.

$-0.00040 \le dn_D/dt\ (°C^{-1}) \le -0.00036$ and $-1.13 \le d\rho/dt\ (kg\ m^{-3}\ °C^{-1}) \le -0.84$, respectively. These temperature coefficients correspond to the b_i's ones in eqs 1 and 2, as can be seen in Table 3.

Equations 1−3 were also used to correlate formamide + (formic acid, or + acetic acid, or + propionic acid) binary systems. But in this case, their parameters are also dependent on the mole fraction of formamide (x_F). Consequently, these equations were modified as follows:

$$\rho = a_1(x_F) + b_1(x_F) \times t \quad (4)$$

$$n_D = a_2(x_F) + b_2(x_F) \times t \quad (5)$$

$$\eta = a_3(x_F) \exp[b_3(x_F)/T] \quad (6)$$

To obtain the correlations proposed in eqs 4−6, densities and refractive indexes of the mixtures were plotted against t, while the viscosity data were plotted against $1/T$. Figure 1 shows the plot of the density for the (F + FA) binary system, keeping x_F as a parameter. All systems and properties show straight lines for each composition, except for viscosity. From these plots, and using the same regression methods stated above for pure components, the parameters $a_i(x_F)$ and $b_i(x_F)$ were obtained. They are plotted against the mole fraction of formamide (x_F), as can be seen in Figures 2 and 3 for the same binary system, to obtain its composition dependence. Since the plots for the other properties and systems are similar, they are not presented here.

The resulting equations for the density, refractive index, and viscosity of the three binary systems are collected in Table 4, in which the $a_i(x_F)$ and $b_i(x_F)$ coefficients are presented together with their standard deviations (σ).

Equations 7−15 make it possible to predict the density, viscosity, and refractive index of these binary systems at any composition and temperature (in the temperature range studied). The values calculated with these equations compare well with the experimental data.

As can be seen, and following Eyring's theory,[6] the correlations for viscosity are functionally different from those of the other two parameters studied in this work, both for pure components and for binary mixtures. This is in agreement with many other works.[7−11]

Literature Cited

(1) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.
(2) Lide, D. R.; Kehiaian, H. V. *CRC Handbook of Thermophysical and Thermochemical Data*; CRC Press: Boca Raton, FL, 1994.

(3) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 69th ed.; CRC Press: Boca Raton, FL, 1988.
(4) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in C*, 2nd ed.; Cambridge University Press: 1992.
(5) Ortega, J. Density and Refractive Indices of Pure Alcohols as a Function of Temperature. *J. Chem. Eng. Data* **1982**, *27*, 312−317.
(6) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941.
(7) D'Aprano, A.; Donato, I. D.; Turco Liberi, V. Molecular Interactions in 1-Pentanol + 2-Methyl-2-butanol Mixtures: Static Dielectric Constant, Viscosity and Refractive Index Investigations at 5, 25 and 45 °C. *J. Solution Chem.* **1989**, *18*, 785−793.
(8) Frej, H.; Baliñska, A.; Jakubczyk, M. Density and Viscosity of Undersaturated, Saturated, and Supersaturated Aqueous Ammonium Oxalate Solutions from 287 K to 325 K. *J. Chem. Eng. Data* **2000**, *45*, 415−418.
(9) Ku Hsu-Chen; Tu Chein-Hsiun. Densities and Viscosities of Seven Glycol Ethers from 288.15 K to 343.15 K. *J. Chem. Eng. Data* **2000**, *45*, 391−394.
(10) Riggio, R.; Martínez, H. E.; Espindola, H. E.; Ramos, J. F. Viscosities, Densities, and Refractive Indexes of Mixtures of Methyl Isobutyl Ketone-Isobutyl Alcohol. *J. Chem. Eng. Data* **1984**, *29*, 11−13.
(11) Riggio, R.; Martínez, H. E.; Sólimo, H. N. Densities, Viscosities, and Refractive Indexes for the Methyl Isobutyl Ketone + Pentanols Systems. Measurements and Correlations. *J. Chem. Eng. Data* **1986**, *31*, 235−238.

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