

Vapour pressure and excess Gibbs free energy of the ternary system $\{x_1\text{CH}_3\text{F} + x_2\text{HCl} + x_3\text{N}_2\text{O}\}$ at temperature of 182.33 K

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Abstract

The equilibrium pressure of ternary mixtures of $\{x_1\text{CH}_3\text{F} + x_2\text{HCl} + x_3\text{N}_2\text{O}\}$ covering the entire composition range has been measured at temperature of 182.33 K by the static method. The system exhibits a minimum pressure for the binary $\{x_1\text{CH}_3\text{F} + x_2\text{HCl}\}$. The molar excess Gibbs free energy has been calculated from the experimental equilibrium pressure. For the equimolar mixture $G_m^E(x_1 = x_2 = x_3 = 1/3) = (-297 \pm 20) \text{ J} \cdot \text{mol}^{-1}$. The (p, x, y) surface for the ternary system and the corresponding curves for the three constituent binary mixtures obtained from the Peng–Robinson equation of state are in agreement with the experimental data.

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1. Introduction

For many years now we have been reporting on the primary thermodynamic excess functions (G^E , H^E , S^E , and V^E) and on the equilibrium pressure of cryogenic systems involving molecularly simple components. The experimental technique used in these studies for binary liquid mixtures was introduced by L.A.K. Staveley in Oxford [1,2]. It was extended to ternary systems not long ago in our laboratory in Coimbra [3,4]. The soundness of this technique derives from two basic features: firstly, the components used either for preparing the mixtures or for providing the cryogenic (thermostatic) medium are submitted to previous thorough purification; and secondly, the measurements are taken at a constant low-temperature provided by a pure substance melting slowly in the cryostat at its own triple-point. This is, of course, a physical invariant of the substance and therefore the temperature at which the measurements are taken does not depend upon the precision of any thermostatic device but only on the nature and purity of the cryogenic substance chosen for the exper-

iments. As far as we are aware measurements on ternary mixtures of liquefied gases under such conditions have not been carried out regularly in other laboratories. The main objective of our studies has been to provide reliable data on which theories of liquid mixtures can be tested. For this reason most of the systems selected so far for these studies involve components of small, rigid molecules whose intermolecular potential parameters are known with sufficient precision. In this context molecular polarity is, of course, one of the main features to be taken into account in the selection of the components of the system to be studied, as well as the possibility of hydrogen bonding, a subject on which we have reported recently [5–7]. In this work we examine the ternary mixture $\{x_1\text{CH}_3\text{F} + x_2\text{HCl} + x_3\text{N}_2\text{O}\}$ at $T = 182.33 \text{ K}$, the triple-point temperature of dinitrogen oxide (nitrous oxide). This is the lowest temperature at which the three components are liquid, since the triple-point temperature of both methyl fluoride and hydrogen chloride are lower than that of N_2O [8]. Having studied $\{x_1\text{CH}_3\text{F} + x_2\text{N}_2\text{O} + x_3\text{Xe}\}$ at the same temperature [3] the substitution of Xe for HCl as the third component in the mixture provides a more stringent example on which theories can be tested, since hydrogen chloride molecules possess non-negligible dipole and quadrupole

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moments ($\mu = 3.57 \times 10^{-30} \text{ C} \cdot \text{m}$ and $Q = 12.7 \times 10^{-40} \text{ C} \cdot \text{m}^2$, respectively) [9], and also can hydrogen bond to the molecules of CH_3F as suggested in one of our previous studies [5]. In the next sections we report on the experiments and calculations made to determine the molar excess Gibbs free energy of $\{x_1\text{CH}_3\text{F} + x_2\text{HCl} + x_3\text{N}_2\text{O}\}$. Methyl fluoride has a relatively large dipole moment ($\mu = 6.20 \times 10^{-30} \text{ C} \cdot \text{m}$) but almost no quadrupole ($Q = 0.12 \times 10^{-40} \text{ C} \cdot \text{m}^2$), while the situation with nitrous oxide is quite the opposite: $\mu = 0.55 \times 10^{-30} \text{ C} \cdot \text{m}$; $Q = 12.3 \times 10^{-40} \text{ C} \cdot \text{m}^2$ [9].

2. Experimental

The apparatus and the technique used to measure the total equilibrium pressure of ternary liquefied gas mixtures have been described [3]. And the same for the uncertainties associated to the subsequent calculations [4]. Each of the substances used either as component of the mixtures to be studied or for the cryostat were further purified by fractionation in the laboratory low-temperature column, the middle fraction being used in the experiments. In this work the original samples were supplied as cylinder gases with stated molar purity greater than 0.995: methyl fluoride from Linde, and both hydrogen chloride and dinitrogen oxide from Matheson. The final purity of the samples used in the experiments was confirmed by examining the constancy of their respective triple-point pressure during melting, as measured with a wide-bore standard mercury-in-glass manometer. Corrections of the raw-readings from the manometer were made for latitude, altitude, temperature, and bore diameter of the glass U-tube as usual [10]. The triple-point pressures so obtained are compared in table 1 with values taken from the literature.

The ternary mixtures were prepared from each of the binaries by adding rigorously measured quantities of the third component as described previously [3]. No sampling of the equilibrium phases is needed. The uncertainties attached to the raw data and to the derived quantities have been extensively examined and reported before [3,4].

The evaluation of G_m^E from the raw data needs some ancillary values, which we shall summarize briefly. To account for the nonideality in the gas phase second virial coefficients were taken from the compilation of Dymond and Smith [13] and fitted to the equation:

$$B/V_c = \sum_{i=0}^3 b_i T_r^{-i}, \quad (1)$$

where V_c is the molar critical volume, $T_r = T/T_c$ is the reduced temperature, and the b_i are parameters. In the absence of experimental information the values of the cross second virial coefficients B_{ij} were assumed to be the arithmetic means of the values for the pure components. No significant error should be introduced in the final results by this assumption concerning second order correction terms. As for the molar volumes of the pure liquid components at $T = 182.33 \text{ K}$, which are needed in the calculation of G_m^E , the following values were used: $V_{m,1} = (37.526 \pm 0.026) \text{ cm}^3 \cdot \text{mol}^{-1}$ [12]; $V_{m,2} = (30.413 \pm 0.005) \text{ cm}^3 \cdot \text{mol}^{-1}$ [10]; $V_{m,3} = (35.487 \pm 0.002) \text{ cm}^3 \cdot \text{mol}^{-1}$ [10]. Throughout this paper methyl fluoride is designated as component 1, hydrogen chloride as component 2, and dinitrogen oxide as component 3. All the experiments were carried out at $T = 182.33 \text{ K}$.

3. Results

As said, the three binary mixtures involving CH_3F , HCl , and N_2O as components can be studied as liquids at $T = 182.33 \text{ K}$ over their complete composition ranges. Independent measurements on $\{x_2\text{HCl} + x_3\text{N}_2\text{O}\}$, taken in the Oxford laboratory [14], provide accurate VLE and $G_{ij,m}^E$ values that can be used to test the experimental results on which we are reporting in the present work. A less stringent evaluation of these results is obtained by comparison with previous studies on $\{x_1\text{CH}_3\text{F} + x_3\text{N}_2\text{O}\}$ [15], and on $\{x_1\text{CH}_3\text{F} + x_2\text{HCl}\}$ [5] carried out in our (Coimbra) laboratory recently. Those from reference [15] were chosen for such purpose since the observations were made by a different experimenter.

3.1. The binary system $\{x_1\text{CH}_3\text{F} + x_3\text{N}_2\text{O}\}$

The equilibrium pressure p has been measured for 12 mixtures of methyl fluoride and dinitrogen oxide at $T = 182.33 \text{ K}$. The experimental results are shown in table 2 and in figures 1 and 2. The values of $G_{13,m}^E$ have been obtained using Barker's method [16], assuming for the molar excess Gibbs free energy a three-term equation of the form

$$G_{ij,m}^E/(RT) = x_i x_j \{A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2\}, \quad (2)$$

where $i = 1$; $j = 3$. The values obtained for the parameters are: $A_{13} = 0.1231 \pm 0.0102$; $B_{13} = -0.0918 \pm 0.0052$; $C_{13} = 0.0728 \pm 0.0320$. For the equimolar mixture $G_{13,m}^E(x_1 = 0.50) = (46.7 \pm 3.9) \text{ J} \cdot \text{mol}^{-1}$. These values are to be compared with $A_{13} = 0.1248 \pm 0.0057$; $B_{13} = -0.0862 \pm 0.0034$; $C_{13} = 0.0645 \pm 0.0164$, and $G_{13,m}^E(x_1 = 0.50) = (48.5 \pm 2.2) \text{ J} \cdot \text{mol}^{-1}$ reported by Fonseca and Lobo [15]. The agreement is much satisfactory as seen in the above mentioned plots (figures 1 and 2).

TABLE 1
Triple-point pressures p_i of the substances used in this work

Substance	T_i/K	p_i/kPa		Reference
		This work	Literature	
CH_3F	130.46 ^a	0.375 ± 0.015	0.379 ± 0.003 0.400 ± 0.005	[11] [3]
HCl	159.01	13.793 ± 0.035	13.811 ± 0.009	[8]
N_2O	182.33	87.951 ± 0.015	87.895 ± 0.007 87.865 ± 0.012	[11] [8]

T_i is the triple-point temperature [8].

^a Taken from reference [12].

TABLE 2

Experimental vapour pressure p and molar excess Gibbs free energy $G_{13,m}^E$ as a function of composition for the system $\{x_1\text{CH}_3\text{F} + x_3\text{N}_2\text{O}\}$ at $T = 182.33\text{ K}$

x_1	y_1	p/kPa	$\Delta p/\text{kPa}$	$G_{13,m}^E/(\text{J} \cdot \text{mol}^{-1})$
0	0	87.875 ^a		0
0.1556	0.0887	83.621	+0.004	44.1
0.3199	0.2084	77.484	-0.484	46.5
0.3984	0.2648	74.646	-0.246	48.5
0.4074	0.2706	74.592	+0.056	53.1
0.5454	0.3870	68.940	+0.278	47.9
0.5586	0.4028	67.783	-0.283	37.7
0.6708	0.5178	63.120	+0.030	34.0
0.7053	0.5562	61.731	+0.173	33.6
0.7968	0.6719	57.568	+0.086	24.5
0.8128	0.6946	56.766	-0.005	21.6
0.8878	0.8032	53.453	+0.038	15.1
0.8898	0.8108	53.064	-0.253	10.1
1	1	48.163 ^b		0

x_1 and y_1 are the mole fractions of CH_3F in the liquid and in the vapour, respectively. $\Delta p (=p - p_{\text{calc}})$ are the pressure residuals.

^a Value reported in reference [15].

^b Value from reference [3].

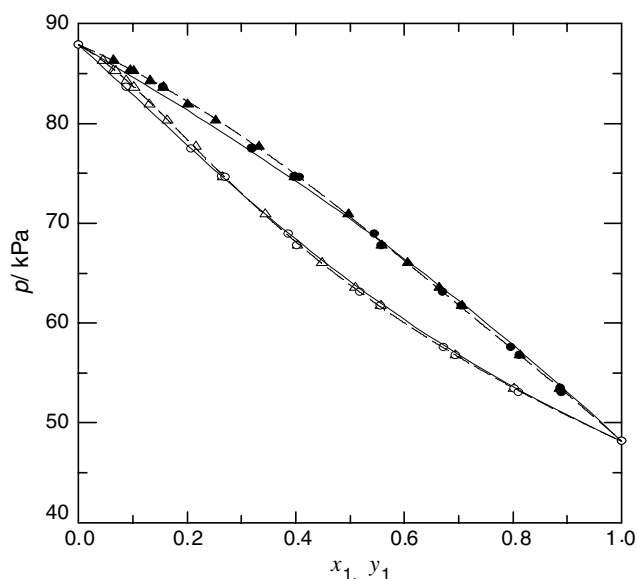


FIGURE 1. Vapour pressure p of the system $\{x_1\text{CH}_3\text{F} + x_3\text{N}_2\text{O}\}$ at temperature of 182.33 K. x_1 and y_1 are, respectively, the mole fraction of CH_3F in the liquid phase and in the vapour phase. The symbols represent experimental values: the circles are for this work, and the triangles are from reference [15]. The open symbols are for the vapour and the full symbols refer to the liquid phase. The equilibrium (p, x_1) and (p, y_1) full lines are from experiment, using equation (2); the dashed lines are calculated from equation (5).

3.2. The binary system $\{x_2\text{HCl} + x_3\text{N}_2\text{O}\}$

The results obtained in this work for the equilibrium pressure p are compiled in table 3, and the (p, x, y) and (G_m^E, x) diagrams are plotted in figures 3 and 4. The values of the parameters in equation (2), with $i = 2$ and $j = 3$, for this binary mixture at $T = 182.33\text{ K}$, the temperature at which our study has been carried out, are: $A_{23} =$

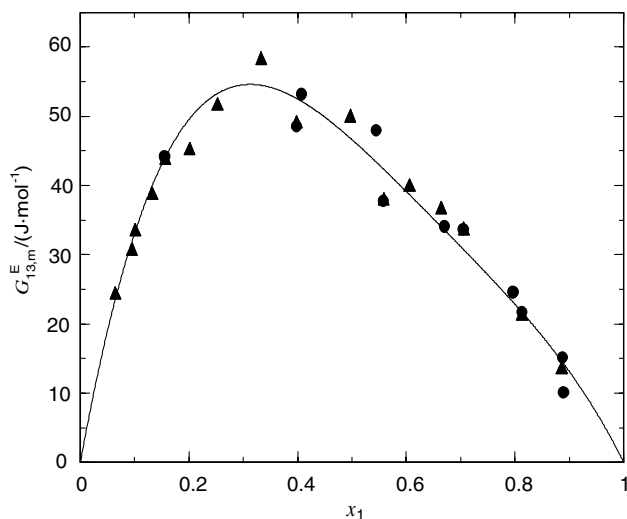


FIGURE 2. Molar excess Gibbs free energy $G_{13,m}^E$ for the system $\{x_1\text{CH}_3\text{F} + x_3\text{N}_2\text{O}\}$ as a function of methyl fluoride mole fraction in the liquid, x_1 . Circles are for this work; triangles were taken from Fonseca and Lobo [15]. The line represents $G_{13,m}^E$ calculated from equation (2).

TABLE 3

Experimental vapour pressure p and molar excess Gibbs free energy $G_{23,m}^E$ as a function of composition for the system $\{x_2\text{HCl} + x_3\text{N}_2\text{O}\}$ at $T = 182.33\text{ K}$

x_2	y_2	p/kPa	$\Delta p/\text{kPa}$	$G_{23,m}^E/(\text{J} \cdot \text{mol}^{-1})$
0	0	87.875 ^a		0
0.0786	0.0887	89.579	+0.592	76.0
0.1899	0.1952	89.716	-0.079	85.7
0.2339	0.2332	89.947	+0.034	102.4
0.2412	0.2390	90.182	+0.255	108.3
0.4058	0.3771	89.325	+0.003	139.5
0.4583	0.4212	88.719	-0.104	143.1
0.4644	0.4270	88.512	-0.239	141.4
0.6009	0.5452	86.103	-0.586	135.2
0.6113	0.5522	86.244	-0.253	139.4
0.6546	0.5862	85.977	+0.379	143.4
0.6911	0.6202	84.970	+0.251	134.9
0.7446	0.6738	83.104	-0.140	116.4
0.9034	0.8441	77.904	+0.581	62.5
0.9280	0.8820	76.307	+0.176	44.5
1	1	72.134 ^b		0

x_2 and y_2 are the mole fractions of HCl in the liquid and in the vapour, respectively. $\Delta p (=p - p_{\text{calc}})$ are the pressure residuals.

^a Value reported in reference [15].

^b Taken from reference [14].

0.3800 ± 0.0077 ; $B_{23} = 0.0350 \pm 0.0034$; $C_{23} = 0.0774 \pm 0.0281$. For the equimolar mixture we found $G_{23,m}^E(x_2 = 0.50) = (144.0 \pm 2.9)\text{ J} \cdot \text{mol}^{-1}$.

Lobo and Staveley [14] also measured the equilibrium pressure p for $\{x_2\text{HCl} + x_3\text{N}_2\text{O}\}$, and reported on the molar excess Gibbs free energy $G_{23,m}^E$ for this system at the same temperature. They arrived at: $A_{23} = 0.3875 \pm 0.0022$; $B_{23} = -0.0171 \pm 0.0045$; $C_{23} = 0.0209 \pm 0.0108$, and $G_{23,m}^E(x_2 = 0.50) = (146.9 \pm 0.8)\text{ J} \cdot \text{mol}^{-1}$. The accordance between the two sets of results is reassuring.

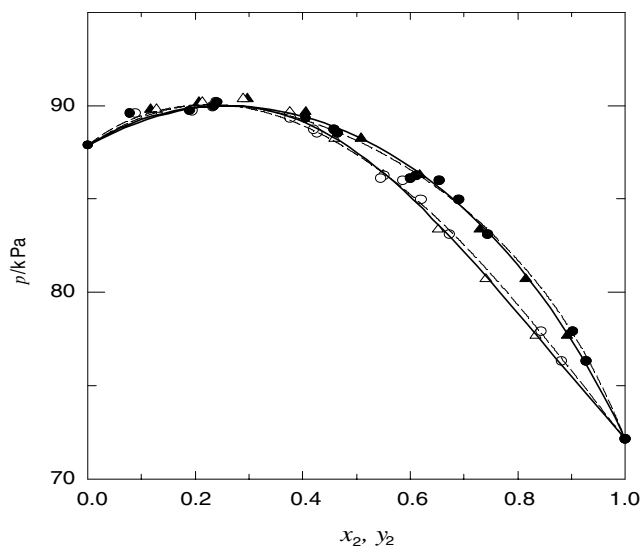


FIGURE 3. Vapour pressure p of the system $\{x_2\text{HCl} + x_3\text{N}_2\text{O}\}$ at temperature of 182.33 K. x_2 and y_2 are, respectively, the mole fraction of HCl in the liquid phase and in the vapour phase. The symbols represent experimental values: the circles are for this work, and the triangles are from reference [14]. The open symbols are for the vapour and the full symbols refer to the liquid phase. The equilibrium (p, x_2) and (p, y_2) full lines are from experiment, using equation (2); the dashed lines are calculated from equation (5).

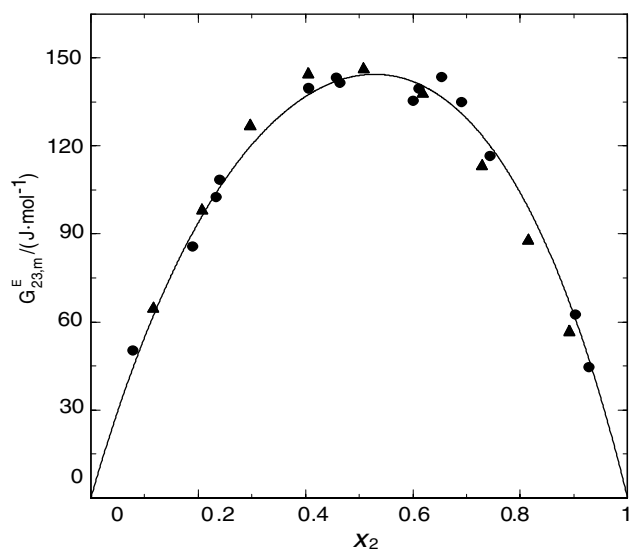


FIGURE 4. Molar excess Gibbs free energy $G_{23,m}^E$ for the system $\{x_2\text{HCl} + x_3\text{N}_2\text{O}\}$ as a function of x_2 , the mole fraction of HCl in the liquid. Circles are for this work; triangles are from Lobo and Staveley [14]. The line represents $G_{23,m}^E$ calculated from equation (2).

3.3. The binary system $\{x_1\text{CH}_3\text{F} + x_2\text{HCl}\}$

We have studied recently the binary mixture of methyl fluoride and hydrogen chloride at $T = 182.33$ K [5]. The parameters in equation (2), with $i = 1$ and $j = 2$, are: $A_{12} = -2.2332 \pm 0.0389$; $B_{12} = 0.4082 \pm 0.0087$; $C_{12} = 0.5027 \pm 0.0796$. For the equimolar mixture $G_{12,m}^E(x_1 = 0.50) = (-846.4 \pm 14.7) \text{ J} \cdot \text{mol}^{-1}$. We are not aware

of any other measurements on this system to be compared with ours.

3.4. The ternary mixture $\{x_1\text{CH}_3\text{F} + x_2\text{HCl} + x_3\text{N}_2\text{O}\}$

The experimental results obtained for 52 ternary mixtures at $T = 182.33$ K are registered in table 4. In the

TABLE 4

Vapour pressure p and molar excess Gibbs free energy G_m^E as a function of composition for the system $\{x_1\text{CH}_3\text{F} + x_2\text{HCl} + x_3\text{N}_2\text{O}\}$ at $T = 182.33$ K

x_1	x_2	y_1	y_2	p/kPa	$\Delta p/\text{kPa}$	$G_m^E/(\text{J} \cdot \text{mol}^{-1})$
0.0818	0.7527	0.0105	0.7068	75.213	+0.270	-130.1
0.0897	0.8231	0.0107	0.8192	69.864	-0.814	-225.5
0.1072	0.6656	0.0167	0.6046	76.712	+1.010	-134.3
0.1076	0.4140	0.0266	0.3484	81.437	-0.523	-39.0
0.1281	0.1670	0.0560	0.1377	82.978	-0.483	+11.4
0.1320	0.8053	0.0186	0.8389	68.150	+2.073	-287.7
0.1361	0.3522	0.0400	0.2868	81.906	+0.925	-30.1
0.1414	0.6583	0.0246	0.6053	71.582	-0.770	-257.9
0.1568	0.0676	0.0876	0.0535	84.482	+1.490	+57.9
0.1584	0.7328	0.0265	0.7315	65.997	-0.660	-368.1
0.1616	0.5075	0.0376	0.4271	76.206	+0.563	-168.0
0.1705	0.7492	0.0294	0.7762	66.131	+2.122	-356.7
0.1786	0.0881	0.0958	0.0665	82.701	+0.821	+35.8
0.1857	0.3795	0.0568	0.2978	77.973	+1.033	-114.2
0.1865	0.0454	0.1099	0.3377	81.859	-0.173	+30.3
0.1963	0.3195	0.0680	0.2428	79.048	+1.572	-78.5
0.2136	0.4251	0.0643	0.3351	72.315	-1.188	-238.3
0.2182	0.1899	0.0984	0.1349	78.122	-0.370	-54.7
0.2205	0.3949	0.0706	0.3045	73.435	-0.392	-207.7
0.2206	0.3691	0.0736	0.2805	74.437	-0.093	-180.4
0.2231	0.3621	0.0757	0.2735	73.345	-1.155	-200.0
0.2244	0.1500	0.1095	0.1045	79.032	+0.163	-24.0
0.2474	0.1926	0.1148	0.1311	75.098	-1.698	-104.3
0.2777	0.4389	0.0966	0.3411	68.184	+0.874	-318.4
0.2818	0.0346	0.1726	0.0212	79.421	+0.844	+46.1
0.2908	0.5183	0.0976	0.4431	61.237	-0.666	-474.9
0.3071	0.3115	0.1327	0.2119	69.206	-0.489	-249.2
0.3406	0.1925	0.1781	0.1154	71.886	+0.416	-129.4
0.3587	0.1132	0.2085	0.0629	75.026	+0.198	-20.6
0.3659	0.0813	0.2211	0.0439	74.828	+1.152	-5.9
0.3784	0.0617	0.2352	0.0324	73.959	+0.261	-6.3
0.3791	0.0468	0.2391	0.0244	74.362	+0.215	+8.7
0.4150	0.4215	0.2238	0.3174	53.228	-0.702	-564.2
0.4184	0.1497	0.2518	0.0788	67.693	-0.757	-151.5
0.4484	0.1755	0.2772	0.0912	64.986	-0.584	-202.2
0.4615	0.2770	0.2840	0.1602	59.003	-0.356	-369.0
0.4687	0.3500	0.2958	0.2281	52.690	-1.109	-527.2
0.4718	0.1335	0.3061	0.0650	65.876	-0.254	-144.6
0.4856	0.1166	0.3220	0.0551	67.939	+1.741	-79.8
0.5112	0.1360	0.3483	0.0635	63.508	-0.265	-167.5
0.5152	0.3284	0.3683	0.2025	51.235	+0.084	-508.4
0.5162	0.0589	0.3576	0.0257	67.294	+0.034	-40.3
0.5520	0.3369	0.4444	0.2111	46.208	-0.675	-592.6
0.5603	0.3576	0.4781	0.2380	44.140	+0.195	-618.6
0.5699	0.0531	0.4136	0.0218	66.194	+1.234	-15.0
0.5820	0.2297	0.4560	0.1132	53.265	-0.233	-381.9
0.5940	0.2884	0.5069	0.1588	49.981	+2.219	-440.3
0.6288	0.1797	0.5161	0.0793	52.680	-1.333	-339.8
0.6305	0.3064	0.6141	0.1759	43.169	+0.399	-570.8
0.6566	0.1761	0.5622	0.0757	52.317	-0.255	-316.3
0.6787	0.0519	0.5423	0.0196	61.145	+1.430	-27.1
0.7836	0.0831	0.7151	0.0302	54.945	+2.500	-78.9

x_i and y_i are the mole fractions of component i in the liquid and in the vapour, respectively. $\Delta p (= p - p_{\text{calc}})$ are the pressure residuals.

TABLE 5
Equation (3) and its parameters

Equation (3)	Parameters
$\frac{G_m^E}{RT} = x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] +$ $x_1x_3[A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2] +$ $x_2x_3[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] +$ $x_1x_2x_3(c_0 - c_1x_1 - c_2x_2)$	$A_{12} = -2.2332 \pm 0.0389; B_{12} = 0.4082 \pm 0.0087; C_{12} = 0.5027 \pm 0.0796$ $A_{13} = 0.1231 \pm 0.0102; B_{13} = -0.0918 \pm 0.0052; C_{13} = 0.0728 \pm 0.0320$ $A_{23} = 0.3800 \pm 0.0077; B_{23} = 0.0350 \pm 0.0034; C_{23} = 0.0774 \pm 0.0281$ $c_0 = -0.3588 \pm 0.2618; c_1 = -0.7007 \pm 0.4864; c_2 = -0.6341 \pm 0.6695$

calculations we assumed that for the three-component mixtures the molar excess Gibbs free energy G_m^E is represented by an equation of the form:

$$G_m^E = \sum_{i < j} \sum_{j=1}^3 G_{ij,m}^E + G_{123,m}^E, \quad (3)$$

where the $G_{ij,m}^E$ for the binary mixtures are given by equation (2) with the values of the parameters stated above, and

$$G_{123,m}^E/(RT) = x_1x_2x_3(c_0 - c_1x_1 - c_2x_2) \quad (4)$$

is a ternary contribution [17]. The parameters c_0 , c_1 , and c_2 have been optimised from ternary data only by using an extension of Barker's method on which we have reported [4]. The values of the parameters in equations (2)–(4) are summarised in table 5. The molar excess Gibbs free energy for the equimolar mixture ($x_1 = x_2 = x_3 = 1/3$) calculated from equation (3) is $G_m^E = (-297 \pm 20) \text{ J} \cdot \text{mol}^{-1}$. Perspective views of the (p, x_i, y_i) and the (G_m^E, x_i) surfaces are shown in figures 5 and 6, respectively. The minimum value

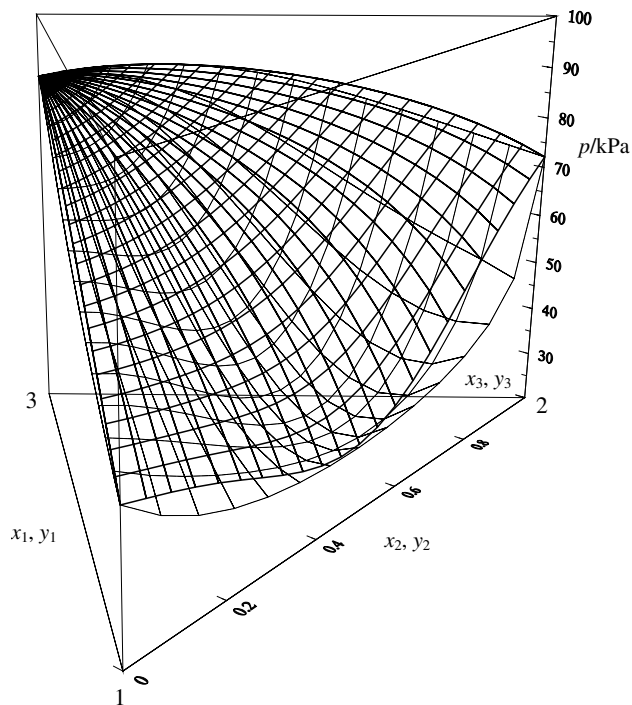


FIGURE 5. Perspective view of the (p, x, y) surfaces for $\{x_1\text{CH}_3\text{F} + x_2\text{HCl} + x_3\text{N}_2\text{O}\}$, at $T = 182.33 \text{ K}$. Full lines are for the liquid; thinner lines are for the vapour.

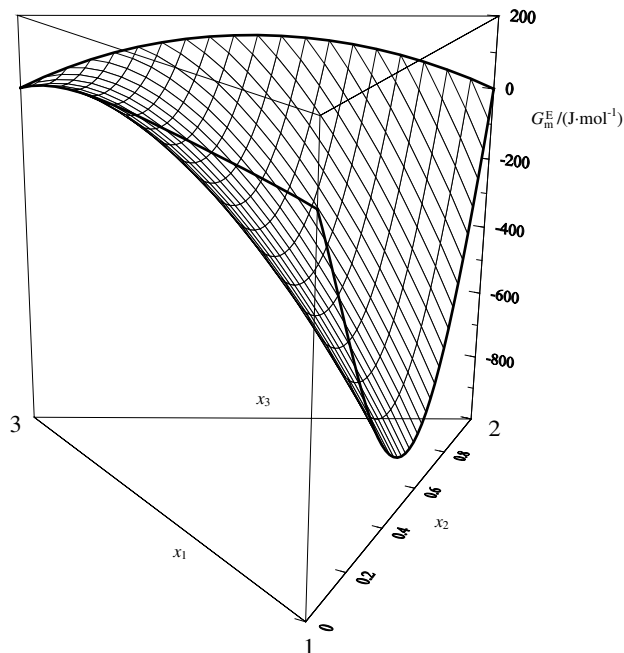


FIGURE 6. Perspective view of the (G_m^E, x_i) surface for $\{x_1\text{CH}_3\text{F} + x_2\text{HCl} + x_3\text{N}_2\text{O}\}$, at $T = 182.33 \text{ K}$.

of G_m^E corresponds to that of the binary mixture of methyl fluoride and hydrogen chloride, owing to the saddle form of the (G_m^E, x_i) surface.

4. Discussion

The highly non-ideal behaviour of the mixtures of $\text{CH}_3\text{F} + \text{HCl}$ showing a negative azeotrope at $x_1 = 0.536$ and a minimum pressure of $p = 33.27 \text{ kPa}$, with high negative values of G_m^E is the result of relatively strong specific forces in the liquid phase, in addition to the interaction between the dipoles and quadrupoles of the two species. We believe that in the liquid mixtures the fluorine atom in CH_3F is involved by hydrogen-bonding with the hydrogen atom in the HCl molecules. The calculations made with simple models of the chemical theories of solutions [5], due to Dolezaleck and to Harris and Prausnitz, suggest that dimerization through an hydrogen-bonded complex between CH_3F and HCl is significant.

The system $\{x_2\text{HCl} + x_3\text{N}_2\text{O}\}$ shows a positive azeotrope at $x_2 \approx 0.23$ and at $p \approx 90.05 \text{ kPa}$, calculated from

the (vapour + liquid) equilibria equations with the Redlich–Kister model for G_m^E . Lobo and Staveley suggested that hydrogen-bonding between the two molecules might be possible [14]. Sufficiently strong hydrogen-bonding would lead to negative values of G^E . However, the values of this property are positive but (perhaps) not high enough to exclude hydrogen-bonding in some extension.

The overall low values of G^E observed for the system $\{\text{CH}_3\text{F} + \text{N}_2\text{O}\}$ indicate a less non-ideal behaviour comparing with the other two systems.

In figure 7, a perspective view of the ternary contribution $G_{123,m}^E$ surface is shown. It is highly unsymmetrical and shows positive values with maxima near the $\{x_1\text{CH}_3\text{F} + x_2\text{HCl}\}$ side. For $\{\text{CH}_3\text{F} + \text{N}_2\text{O} + \text{Xe}\}$ Lobo and Fonseca [17] found that the use of the non-additive ternary contribution $G_{123,m}^E$ in equation (3) makes the distribution of the pressure residuals $\Delta p = (p_{\text{exp}} - p_{\text{calc}})$ much closer to the Gaussian model. The system studied in this work exhibits high negative values of G_m^E near the $\text{CH}_3\text{F} + \text{HCl}$ binary corresponding to the larger values of $G_{123,m}^E$ in the same region. The contrast between the shapes of the two surfaces (cf. figures 6 and 7) leads to conclude that although equation (3) can work as a useful mathematical tool to minimize the pressure residuals and to adjust the G_m^E function to the experimental observations it lacks a sound physical meaning; otherwise the lowest values of $G_{123,m}^E$ (and not the larger ones) should also appear near the $\{x_1\text{CH}_3\text{F} + x_2\text{HCl}\}$ binary mixture for which hydrogen-bonding is plausible. In any case, the relatively low values of $G_{123,m}^E$, not exceeding $10 \text{ J} \cdot \text{mol}^{-1}$, indicate that the ternary contribution in equation (3) might be discarded.

The experimental data have been correlated by using the two-constant Peng–Robinson equation of state [18]:

$$p = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)}. \quad (5)$$

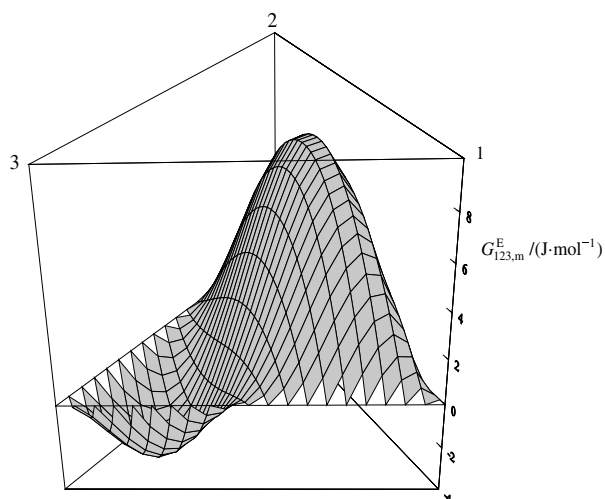


FIGURE 7. Perspective view of the ternary contribution ($G_{123,m}^E, x_i$) surface for $\{x_1\text{CH}_3\text{F} + x_2\text{HCl} + x_3\text{N}_2\text{O}\}$, at $T = 182.33 \text{ K}$.

In this equation p is the pressure, R is the gas constant, T is the temperature, and V_m is the molar volume. The parameters $a(T)$ and b are:

$$a(T) = a(T_c) \times \alpha(T_r, \omega),$$

$$a(T_c) = 0.45724 \times (R^2 T_c^2 / P_c),$$

$$\alpha(T_r, \omega) = [1 + (0.37464 + 1.54266\omega - 0.26992\omega^2) \times (1 - T_r^{0.5})],$$

$$b = 0.07780(RT_c / P_c),$$

where T_c and P_c are the coordinates of the critical point, $T_r (= T/T_c)$ is the reduced temperature, and ω is the Pitzer acentric factor.

To properly correlate phase equilibria equations of state must be able to reproduce pure component vapour pressure accurately. The Peng–Robinson equation predicts the vapour pressure of CH_3F , HCl , and N_2O over the liquid range with deviations of 1.8, 0.5 and 3.0 percent, respectively. To ensure accurate vapour pressures of these substances we have used $a(T) = a(T_c) \times \alpha$ with α being determined from the vapour pressure data of each pure substance at $T = 182.33 \text{ K}$. The values of α obtained are 1.3458, 1.3006, and 1.3122 for methyl fluoride, hydrogen chloride, and nitrous oxide, respectively. The van der Waals one-fluid mixing rules

$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad (6)$$

$$b = \sum_i x_i b_{ii} \quad (7)$$

and the combining rule

$$a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - k_{ij}) \quad (8)$$

have been used. The interaction parameter k_{ij} was obtained by minimizing the sum of the least squares deviations in the predicted bubble point pressure by using the experimental temperature, pressure and liquid phase composition. The reliability of the calculations was assessed by using the average absolute deviation (AAD) defined as

$$\text{AAD} = (1/N) \sum_i 100 [(X_{\text{calc}} - X_{\text{exp}}) / X_{\text{exp}}]_i, \quad (9)$$

where X is the value of vapour pressure or mole fraction of i th point in the vapour phase and N is the number of points.

For the system $\{x_1\text{CH}_3\text{F} + x_2\text{HCl}\}$ the Peng–Robinson equation leads to the optimal value of $k_{12} = -0.152$. With this value of k_{12} the calculated (p, x, y) curve is in satisfactory agreement with experiment [5]. The AAD values are 2% and 6%, respectively, for the calculated equilibrium pressure and the molar fraction of CH_3F in the vapour phase. The experimental negative azeotrope at $x_1 \approx 0.54$ and $p \approx 33.3 \text{ kPa}$ are to be compared with $x_1 \approx 0.56$ and $p \approx 34.5 \text{ kPa}$ obtained from the Peng–Robinson equation of state. For the system $\{x_1\text{CH}_3\text{F} + x_3\text{N}_2\text{O}\}$ the (p, x, y) data of Fonseca and Lobo [15] and those from this work were used. The optimal value of $k_{13} = 0.008$ has been found. As can be seen in figure 1 the calculated and experimental

equilibrium data are in excellent agreement. The AAD values are 0.7% and 2.2%, respectively, for the pressure and the molar fraction of CH_3F in the vapour phase.

The results for the system $\{x_2\text{HCl} + x_3\text{N}_2\text{O}\}$ are presented in figure 3. The optimal value of $k_{23} = 0.026$ has been obtained from the experimental data in this work and the data of Lobo and Staveley [14]. The AAD values for the calculated equilibrium pressure and molar fraction of hydrogen chloride in the vapour phase are 0.3% and 0.6%, respectively. In this system a positive azeotrope at $x_2 \approx 0.23$ and $p \approx 90.1$ kPa is observed, which is to be compared with $x_2 \approx 0.24$ and $p \approx 90.0$ kPa obtained from the Peng–Robinson equation of state.

The interaction parameters k_{ij} found for the binary systems were used to estimate the (p, x, y) equilibrium of the $\{\text{CH}_3\text{F} + \text{HCl} + \text{N}_2\text{O}\}$ ternary system. The AAD deviation from the data in table 4 is 1.5% for the equilibrium pressure, with maxima of 4.5% for p , and 4% for the mole fraction.

In conclusion, the Peng–Robinson equation of state can be used to accurately correlate the data for the ternary system by using information obtained from the constituent binary systems.

We hope that these results may be of use to test theories.

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References

- [1] V. Mathot, L.A.K. Staveley, J.A. Young, N.G. Parsonage, *Trans. Faraday Soc.* 52 (1956) 1488–1500.
- [2] R.H. Davies, A.G. Duncan, G. Saville, L.A.K. Staveley, *Trans. Faraday Soc.* 63 (1967) 855–869.
- [3] I.M.A. Fonseca, L.Q. Lobo, *Fluid Phase Equilib.* 113 (1995) 127–138.
- [4] I.M.A. Fonseca, L.Q. Lobo, *Fluid Phase Equilib.* 154 (1999) 205–211.
- [5] A.M.P. Senra, I.M.A. Fonseca, A.G.M. Ferreira, L.Q. Lobo, *J. Chem. Thermodyn.* 34 (2002) 1557–1566.
- [6] A.M.P. Senra, I.M.A. Fonseca, L.Q. Lobo, *J. Chem. Thermodyn.* 35 (2003) 1051–1057.
- [7] A.M.P. Senra, I.M.A. Fonseca, L.Q. Lobo, *J. Chem. Thermodyn.* 37 (2005) 627–630.
- [8] L.A.K. Staveley, L.Q. Lobo, J.C.G. Calado, *Cryogenics* 21 (1981) 131–144.
- [9] C.G. Gray, K.E. Gubbins, *Theory of Molecular Fluids*, vol. 1, Oxford University Press, New York, 1980.
- [10] L.Q. Lobo, An experimental study of the thermodynamic properties of molecularly simple liquid mixtures, D.Phil. Thesis, University of Oxford, 1979.
- [11] I.M.A. Fonseca, L.Q. Lobo, *Fluid Phase Equilib.* 47 (1989) 249–263.
- [12] I.M.A. Fonseca, L.Q. Lobo, *Rev. Port. Quím.* 31 (1989) 118–121.
- [13] J.H. Dymond, E.B. Smith, *The Virial Coefficients of Pure Gases and Mixtures*, Clarendon, Oxford, 1980.
- [14] L.Q. Lobo, L.A.K. Staveley, *J. Chem. Thermodyn.* 16 (1984) 653–659.
- [15] I.M.A. Fonseca, L.Q. Lobo, *J. Chem. Thermodyn.* 26 (1994) 647–650.
- [16] J.A. Barker, *Aust. J. Chem.* 6 (1953) 207–210.
- [17] L.Q. Lobo, I.M.A. Fonseca, *Mol. Phys.* 80 (1993) 789–792.
- [18] D.Y. Peng, D.B. Robinson, *Ind. Eng. Chem. Fundam.* 15 (1976) 59–64.

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