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Isobaric vapour–liquid equilibria for some halogen-containing ethanes in binary mixtures with HF

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Abstract

The vapour–liquid equilibria (VLE) of four binary mixtures of HF with CCl_2F-CF_2Cl, $CHCl_2-CF_3$, CH_2Cl-CF_3 and CH_2F-CF_3, respectively, have been studied under isobaric conditions. Experimental results have been interpreted by the NRTL (Not Random Two Liquids Theory) method with three parameters. The non-ideality and association of the vapour phase has been described with the virial equation. Despite the strong association of the HF molecules, the NRTL method satisfactorily reproduces the vapour–liquid equilibria of the binary mixtures, especially their lack of miscibility.

Introduction

It is known that great efforts are being made to replace Cl with C2 chlorofluorocarbons (CFC) in different uses, with the aim of reducing ozone depletion effects due to chlorine compounds. The necessity of producing environmentally acceptable fluorocarbons has led to a growing interest in defining the physical properties of these new products [1–3]. Fluorinated compounds are produced by reacting chlorinated species with hydrogen fluoride in the presence of suitable catalysts. Hence, reaction mixtures which usually contain residual reagents and fluorinated products need to be separated in a distillation unit. In order to design the separation unit, it is useful to know the VLE of all the binaries occuring in the multicomponent mixtures.

While some papers have been published concerning the VLE of CFC binary mixtures, none has been published on mixtures of CFC with hydrogen fluoride because of the difficulties in handling HF and collecting reliable data in the presence of this substance.

In this work, we have studied the isobaric VLE of four binary mixtures of HF with CCl_2F-CF_2Cl, $CHCl_2-CF_3$, CH_2Cl-CF_3 and CH_2F-CF_3. In some cases, we have observed wide miscibility gaps and, in all cases, strong

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deviations from ideality. The experimental results have been interpreted by applying the three-parameter NRTL (Not Random Two Liquids Theory) model for the liquid phase [4] and the virial equation for the vapour in equilibrium. NRTL theory is well described by Renon and Prausnitz [4].

Despite the strong association of HF molecules [5], we have observed that it is possible to describe the vapour–liquid equilibria of the mixtures, at difference pressures, by using NRTL parameters. The second virial coefficients have been calculated as suggested by Hayden and O'Connell [6].

Experimental

Apparatus, procedure and chemicals

The apparatus employed for the equilibrium runs is shown schematically in Fig. 1. Two reservoirs were separately filled with the two components of the binary mixture to be tested. The equilibrium cell of stainless steel had a volume of 3 l and was completely bathed in a thermostatting fluid. The temperature was kept constant (±0.1 °C) by heating with an electrical resistance and cooling with a refrigerating coil. The pressure of the system was measured through a pressure transducer with 0.02 atm precision. The temperature was measured with a thermocouple dipped in the liquid phase of the binary mixture. The liquid was stirred with a magnedrive stirrer connected to an electrical motor.

Samples were withdrawn, after interrupting the stirring, via the valves V5, V6, V7 (see Fig. 1) from the vapour phase V5 and from the head and the bottom of the liquid V6 and V7 respectively, in order to observe the presence or otherwise of two liquid phases. Samples taken from the vapour and liquid phases were separately fed to alkaline traps for HF measurement. These traps were thermostatted at temperatures higher than that of the

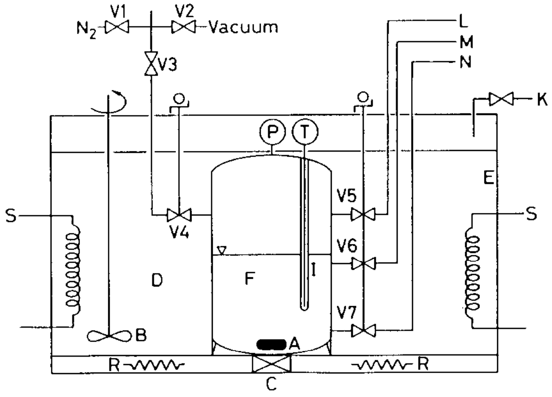


Fig. 1. Schematic representation of the apparatus employed for VLE equilibria measurements: F = equilibrium cell; D = thermostatting fluid; B = fluid bath stirrer; T = thermocouple; P = pressure transducer; V = valves; S = freezing coil; R = electrical resistance heater; C + A = magnetic stirrer; L = vapour sampling line; M, N = liquid sampling lines.

equilibrium cell in order to avoid condensation. For each isobaric run, the pressure, temperature and compositions of both the liquid and vapour phase in equilibrium were measured for nine different mixtures with different molar fractions of 0.1 to 0.9 of one component versus the other. Normally, 1 l of one component was charged into the equilibrium cell and increasing amounts of the other component were added until a molar fraction of *c.* 0.5 was reached; then the procedure was repeated with an inverted sequence. The time elapsed between two experimental measurements was *c.* 4 h, i.e. long enough to reach an equilibrium characterized by pressure constancy.

The fluorinated chemical products used were all produced and supplied by Ausimont SpA, in particular the products Algofrene 113, Meforex 123, HCFC 133a (a laboratory sample) and Meforex 134a were all of 99.9% purity.

Results and discussion

The vapour–liquid equilibrium runs under isobaric conditions were performed on the binary mixtures of HF with the following compounds: CCl_2F-CF_2Cl (CFC113), $CHCl_2-CF_3$(HCFC123), CH_2Cl-CF_3(HCFC133a) and CH_2F-CF_3(HCFC134a). Experimental VLE data for these mixtures are reported in Tables 1–4, respectively. As mentioned above, the data collected have been interpreted with the three-parameters NRTL model [4].

Table 5 reports the thermodynamic data related to the pure components employed for the calculations. Some data listed in the table were estimated by calculation using the methods suggested by Reid, Prausnitz and Sherwood

TABLE 1

Experimental VLE data for the binary system $CCl_2F-CClF_2$ (1) versus HF (2)

$P=1.75$ atm			$P=1.98$ atm		
Temp. (°C)	x_1	y_1	Temp. (°C)	x_1	y_1
34.0	0.000	0.000	37.8	0.000	0.000
26.9	0.030	0.248	31.2	0.030	0.242
26.8	0.060	0.265	30.9	0.050	0.264
27.1	0.200	0.247	30.8	0.150	0.248
26.9	0.300	0.220	30.4	0.250	0.250
26.0	0.400	0.225	29.2	0.390	0.258
25.0	0.500	0.244	29.2	0.500	0.252
25.4	0.600	0.245	30.0	0.600	0.248
25.6	0.700	0.247	29.5	0.700	0.236
25.5	0.850	0.243	29.1	0.800	0.249
24.6	0.960	0.268	29.3	0.900	0.245
64.6	1.000	1.000	29.0	0.960	0.271
			71.0	1.000	1.000

TABLE 2

Experimental VLE data for the binary system $CHCl_2-CF_3$ (1) versus HF (2)

$P=1.05$ atm			$P=3.5$ atm		
Temp. (°C)	x_1	y_1	Temp. (°C)	x_1	y_1
20.1	0.000	0.000	57.5	0.000	0.000
10.8	0.017	0.124	46.8	0.017	0.124
8.5	0.036	0.209	43.7	0.033	0.206
7.4	0.054	0.247	42.1	0.054	0.232
7.4	0.057	0.248	41.8	0.057	0.231
7.5	0.072	0.245	41.7	0.072	0.233
7.5	0.102	0.243	41.8	0.102	0.234
7.6	0.141	0.243	41.7	0.141	0.232
7.4	0.185	0.242	41.6	0.185	0.229
7.4	0.288	0.241	41.8	0.288	0.234
7.5	0.385	0.244	41.6	0.385	0.235
7.6	0.656	0.240	41.8	0.656	0.239
7.5	0.771	0.250	42.0	0.799	0.243
10.1	0.902	0.386	44.2	0.942	0.419
27.8	1.000	1.000	66.0	1.000	1.000

TABLE 3

Experimental VLE data for the binary system CH_2Cl-CF_3 (1) versus HF (2)

$P=3.5$ atm		
Temp. (°C)	x_1	y_1
57.5	0.00	0.000
43.1	0.078	0.193
40.1	0.103	0.231
33.2	0.204	0.336
31.2	0.290	0.430
31.3	0.348	0.435
31.0	0.397	0.433
31.3	0.490	0.433
32.1	0.659	0.565
33.2	0.805	0.721
34.1	0.905	0.845
41.3	1.000	1.000

[7] because they were not available from the literature. Vapour pressure data of pure HCFC 123, 133a and 134a were communicated by Basile [8].

Table 6 shows the NRTL parameters obtained by regression on the experimental data for the different binary mixtures. These parameters must be considered as averaged over the temperature range of the isobar. The quantities Δy and ΔP are absolute mean deviations of y and P, respectively. The fittings obtained for the x/y plots of different binary mixtures by employing

TABLE 4

Experimental VLE data for the binary system CH_2F-CF_3 (1) versus HF (2)

$P=3.0$ atm			$P=10.0$ atm		
Temp. (°C)	x_1	y_1	Temp. (°C)	x_1	y_1
53.0	0.000	0.000	98.0	0.000	0.000
11.5	0.100	0.777	58.1	0.100	0.691
1.8	0.200	0.850	44.4	0.200	0.798
0.8	0.300	0.862	42.0	0.300	0.827
0.4	0.400	0.861	40.5	0.400	0.836
0.1	0.500	0.857	39.4	0.500	0.838
−0.1	0.600	0.852	38.6	0.600	0.840
−0.2	0.700	0.852	38.2	0.700	0.847
−0.2	0.800	0.864	37.8	0.800	0.866
−0.1	0.900	0.902	37.6	0.900	0.908
0.1	0.950	0.940	37.6	0.950	0.945
0.9	1.000	1.000	39.0	1.000	1.000

TABLE 5

Pure component data used in the VLE calculation

$\ln P_i^0 = A + \dfrac{B}{T+C}$ [P_i^0 (bar); T (K)]

	HF	CCl_2F-CF_2Cl	$CHCl_2-CF_3$	CH_2Cl-CF_3	CH_2F-CF_3
M_w (g mol^{-1})	20.006	187.37	152.92	118.49	102.04
T_c (K)	461.15	487.25	457.50	429.80	374.20
P_c (bar)	64.79	34.15	36.09	38.40	40.56
Z_{Ra}	0.1468	0.2723	0.2650	0.2553	0.2458
R_d (Å)	0.2006	3.659	3.273	2.8404	2.4799
D_m (Debye)	1.83	1.8	2.0	2.3	1.82
A	12.5361	9.4025	8.7457	8.7866	9.6385
B	−4389.13	−2657.6	−2116.95	−2012.27	−2008.89
C	57.8280	−38.085	−58.098	−46.674	−37.5538

NRTL with the parameters listed in Table 6 are reported as examples in Figs. 2–5. The dots are the experimental values while the lines are calculated. The fitting obtained for a plot of temperature versus x/y is reported in Fig. 6.

With the exception of HF/CH_2F-CF_3, all the binaries studied show a wide miscibility gap whose extent has been demonstrated experimentally in the manner already described. The conditions for instability can be described via the following relation [4]:

$$\left(\frac{\partial^2 \Delta g^M}{\partial x^2}\right)_{T,P} = 0$$

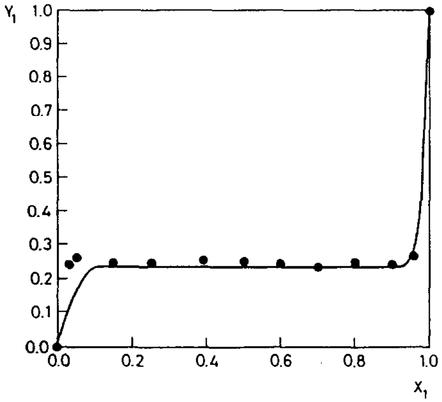
TABLE 6

NRTL parameters determined by regression analysis

CCl_2F-$CClF_2$ (1) versus HF (2) system		
	P = *1.75 atm*	P = *1.98 atm*
Δg_{12}	1855.13 ± 70.51	1828.92 ± 71.71
Δg_{21}	1827.25 ± 101.5	1797.63 ± 99.87
α_{12}	0.41 ± 0.003	0.42 ± 0.004
η_{11}	0.80	0.80
η_{12}	0.50	0.50
η_{22}	1.65	1.65
ΔY	0.0262	0.0249
ΔP (mmHg)	36.60	39.08
$CHCl_2$,CF_3 (1) versus HF (2) system		
	P = *1.05 atm*	P = *3.5 atm*
Δg_{12}	1398.40 ± 64.52	1721.58 ± 46.01
Δg_{21}	1550.95 ± 32.79	1581.27 ± 63.70
α_{12}	0.45 ± 0.002	0.46 ± 0.01
η_{11}	0.80	0.80
η_{12}	0.50	0.50
η_{22}	1.95	2.00
ΔY	0.0273	0.0427
ΔP (mmHg)	16.64	53.65
CH_2Cl-CF_3 (1) versus HF (2) system		
	P = *3.5 atm*	
Δg_{12}	990.01 ± 81.50	
Δg_{21}	598.35 ± 96.60	
α_{12}	0.33 ± 0.09	
η_{11}	0.90	
η_{12}	0.50	
η_{22}	2.00	
ΔY	0.0506	
ΔP (mmHg)	41.31	
CH_2F-CF_3 (1) versus HF (2) system		
	P = *3.0 atm*	P = *10.0 atm*
Δg_{12}	1145.04 ± 20.43	1170.97 ± 33.33
Δg_{21}	1059.10 ± 22.73	1148.50 ± 37.77
α_{12}	0.43 ± 0.002	0.44 ± 0.01
η_{11}	1.40	1.40
η_{12}	0.50	0.50
η_{22}	1.80	1.80
ΔY	0.0305	0.0274
ΔP (mmHg)	27.03	0.07

where Δg^M is the Gibbs molar free energy of mixing and x is the mole fraction of a component in the mixture. By applying this to the Δg^M relation of the NRTL model in the case of a binary system, we have [4]:

$$F(x_1) = -\frac{2\tau_{21}G_{21}^2}{(x_1 + x_2G_{21})^3} - \frac{2\tau_{12}G_{12}^2}{(x_2 + x_1G_{12})^3} + \frac{1}{x_1} + \frac{1}{x_2}$$



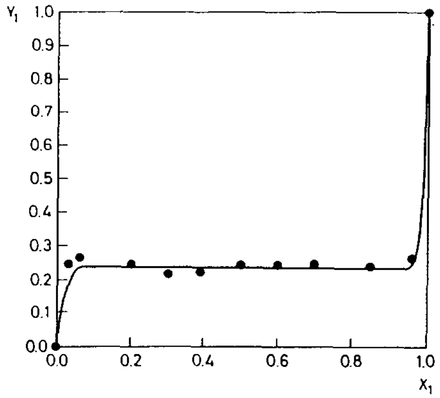
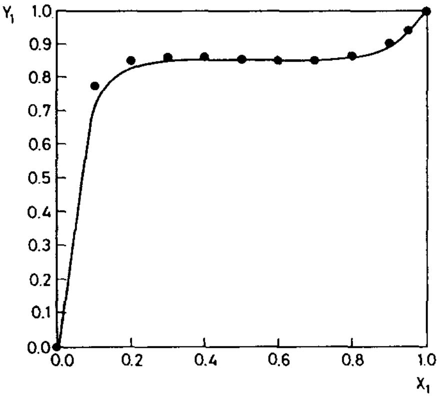


Fig. 2. An x_1/y_1 plot for the system CCl_2F-CF_2Cl (1) versus HF (2) at 1.75 atm pressure.

Fig. 3. An x_1/y_1 plot for the same system as in Fig. 2 at 1.98 atm pressure.



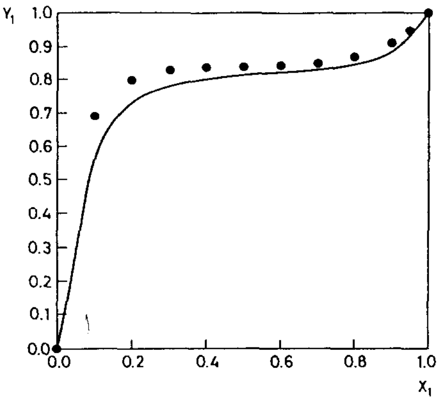


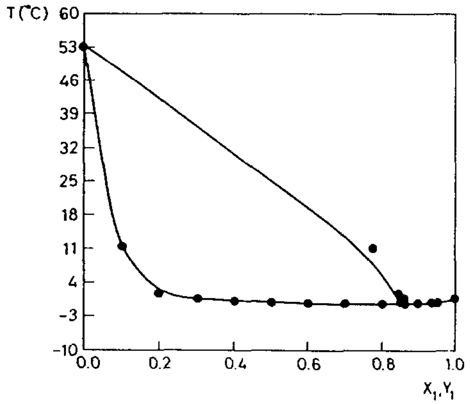
Fig. 4. An x_1/y_1 plot for the system CH_2F-CF_3 (1) versus HF (2) at 3 atm pressure.

Fig. 5. An x_1/y_1 plot for the same system as in Fig. 4 at 10 atm pressure.

This relation, which represents the phase stability, can be plotted as a function of the composition, i.e. as a function of x_1.

The results obtained in our case are reported, as examples, in Figs. 7 and 8. As can be seen, the miscibility gaps observed are hardly affected by temperature. In particular, the HF/CH_2F-CF_3 mixture does not show miscibility gaps at temperatures higher than 0 °C in agreement with the experimental observations.

To conclude, we have shown that it is possible to describe satisfactorily the VLE of HF binary mixtures by employing the NRTL model [4] and the virial equation [5] with parameters that seem to be virtually constant with pressure. The small differences in solvation and association parameters are explained by the change in temperature which is unavoidable in isobaric



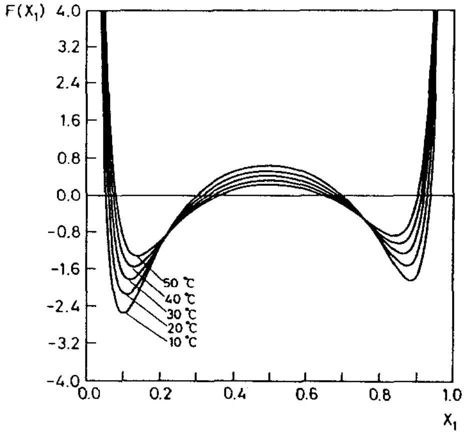


Fig. 6. A temperature versus *x*/*y* plot for the system CH_2F-CF_3 (1) versus HF (2) at 3 atm pressure.

Fig. 7. Phase stability diagram for the system CCl_2F-CF_2Cl (1) versus HF (2) at 1.85 atm pressure.

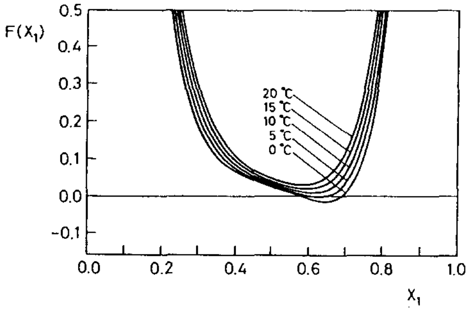


Fig. 8. Phase stability diagram for the system CH_2F-CF_3 (1) versus HF (2) at 3 atm pressure.

runs. Hence, as already mentioned, these parameters must be considered averaged relative to temperature.

Acknowledgement

Thanks are due to Ausimont for financial support.

List of symbols

C_1–C_3	Antoine constants of the vapour pressure
D_m	dipole moment (Debye)
g	Gibbs energy per mol
g_{ij}, g_{ii}	energies of interaction between *ii* and *ij* pairs of molecules

Δg^{M}	Gibbs energy of mixing per mol
Δg_{ij}	$g_{ij}-g_{ii}$
G_{ji}	$\exp(-\alpha_{ji}\tau_{ji})$
M_{w}	molecular weight
P_{c}	critical pressure
R	gas constant
R_{d}	gyration radius
T	absolute temperature
T_{c}	critical temperature
x_i	mole fraction of substance i in liquid phase
y_i	mole fraction of substance i in vapour phase
Z_{Ra}	Rackett parameter

Greek letters

α_{ij}	non-randomness constant for binary ij interactions
η_{ij}, η_{ii}	solution and association parameters, respectively
τ_{ji}	$(g_{ij}-g_{ii})/\mathrm{R}T$

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