p-V_m^l-x,y RELATIONS FOR AZEOTROPIC MIXTURE OF 1,1-DIFLUOROETHANE AND PROPYLENE

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Introduction

1,1-Difluoroethane has come into prominence in the freezing and oil-cleansing industries as one of environmentally the safe fluorocarbons. In refrigerating machines, a mixture consisting of 1,1-difluoroethane (hereafter R-152$_a$) is an important candidate for the refrigerant. However, the physical properties that are basic to the design and operation of the process, namely the phase equilibria including volumetric properties, have not yet been properly investigated.

In the present study, the isothermal vapor-liquid equilibria ($p-x$, y relation) and saturated molar volumes ($V_m^l - x$ relation) of the R-152$_a$-propylene system were measured at 298.15 K by means of a swing method and a weighing method, respectively. The Soave-Redlich-Kwong (SRK) equation of state was used to correlate the experimental $p - V_m^l - x$, y data. It would also be interesting to investigate the applicability of the equation of state to $p-x$, y relations and volumetric properties simultaneously.

1. Eperimental

The phase equilibria ($p-x$, y relation) were measured by means of a static method, the so-called swing method. Equilibrium cells were connected by flexible tubes and the liquid contents were "swung" from one cell to another through a flexible tube by moving the cell up or down. A small amount of sample of each phase was drawn out without disturbing the equilibrium. The composition of each sample was analyzed by gas chromatography. The saturated molar volume of the liquid phase ($V_m^l - x$ relation) was measured by the weighing method, using another apparatus possessing an inner volume of ca. 80 m^3. As the experimental apparatus and procedures used in this study are essentially the same as described in a previous paper,[2] the details are not mentioned here.

The equilibrium pressure was measured with an accuracy of 100 Pa using a quartz Bourdon gage. The temperature was detected by a platinum thermometer within an accuracy of ± 0.01 K.

2. Materials

The propylene was specially supplied by Sumitomo Chemical Co., Ltd., and had a specified minimum purity of 99.96 mol%. The R-152$_a$, obtained from Daikin Ind., Ltd., was research grade with a specified minimum purity of 99.6 mol%. Both chemicals were used without further purification.

3. Results and Discussion

The R-152$_a$-propylene system, which has not been reported in the literature, shows the positive azeotropic behaviour as shown in **Fig. 1**. The equilibrium pressure and mole fraction of propylene at the azeotropic point are interpolated to be 1.187 MPa and 0.872, respectively. **Table 1** summarizes the $p-x$, y data obtained in this study.

The saturated molar volumes of the liquid phase are listed in **Table 2**. As pure propylene was used in the volume calibration of the cell, the value of saturated molar volume was obtained from the literature.[1] The $V_m^l - x$ data were correlated using a Redlich-Kister type equation, also presented in Table 2. Both the pure molar volumes $V_{m,1}$ and $V_{m,2}$ are assumed to be independent of pressure in the
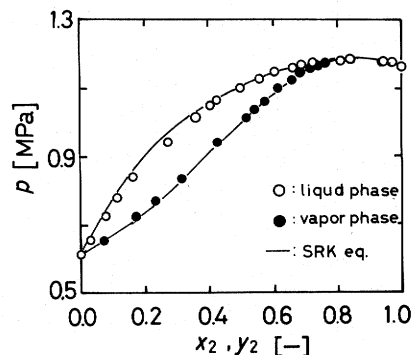

Fig. 1. Vapour-liquid equilibria for the azeotropic mixture of 1,1-difluoroethane (1)-propylene (2) at 298.15 K.

Table 1. Experimental values of $p-x, y$ relation for the 1,1-difluoroethane (1)-propylene (2) system at 25°C

| p [MPa]	x_2 [—]	y_2 [—]
0.6099	0.0000	0.0000
0.6524	0.0329	0.0721
0.7219	0.0789	0.1716
0.7688	0.1166	0.2350
0.8649	0.2027	0.3562
0.9382	0.2806	0.4311
1.0101	0.3638	0.5128
1.0595	0.4305	0.5762
1.0965	0.4994	0.6152
1.1246	0.5595	0.6588
1.1422	0.5959	0.6802
1.1460	0.6049	0.6853
1.1632	0.6631	0.7252
1.1708	0.6870	0.7395
1.1727	0.7129	0.7574
1.1797	0.8026	0.8235
1.1840	0.8389	0.8504
1.1799	0.9415	0.9371
1.1744	0.9761	0.9726

Table 2. Experimental values of $V_m^l - x$ relation for the 1,1-difluoroethane(1)-propylene(1) system at 25°C

x_2 [—]	V_m^l [cm³/mol]
0.0000	73.92
0.1929	75.86
0.3173	77.72
0.4771	79.46
0.5032	79.67
0.7354	81.86
0.8672	83.08
0.9392	83.15
1.0000	83.39

$$V_m^l = V_{m,1}^l x_1 + V_{m,2}^l x_2 - (-0.6181 - 6.277 x_2) x_1 x_2$$

correlation, as the saturated pressure difference between R-152$_a$ and propylene is not so large.

The SRK equation[5] was applied to the $p-x, y$ data using a binary parameter k_{ij} in the interaction term of the mixing rule. The parameters Ω_a and Ω_b in the SRK equation were evaluated from the saturated pressure and liquid density data for each component ($\Omega_{a,1} = 0.37350$, $\Omega_{b,1} = 0.07284$, $\Omega_{a,2} = 0.40736$, and $\Omega_{b,2} = 0.08117$). The critical properties and acentric factor of each substance were obtained from "Property Data Bank".[4] As Fig. 1 shows, the $p-x, y$ relation is satisfactorily correlated with the value of $k_{ij} = 0.10026$. Also, the $V_m^l - x$ relation is expressed well by the SRK equation using the same value of k_{ij}. To
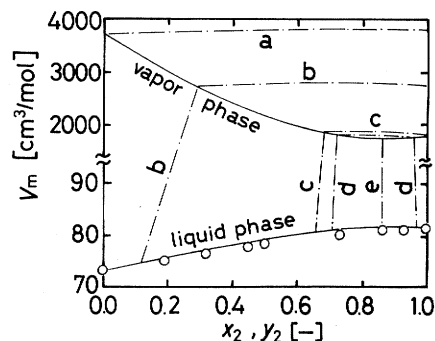
Fig. 2. Volumetric properties of the 1,1-difluoroethane (1)-propylene (2) system at 298.15 K
—: saturated molar volume calculated by SRK eq.
—·—: isobaric curve calculated by SRK eq.
a: p_1^{sat}; b; $p = 0.8$ MPa, c: p_2^{sat}; d: $p = 1.18$ MPa, e: p^{azeo}.

reveal the full volumetric properties of the azeotropic mixture, the isothermal $V_m^l - V_m^g - x, y$ relation is shown in **Fig. 2**, where the volumetric property in the gas phase was estimated by the SRK equation.

Nomenclature

k_{ij}	= binary parameter in SRK equation	[—]
p	= pressure	[MPa]
V_m	= molar volume	[cm³ mol⁻¹]
x	= mole fraction of liquid phase	[—]
y	= mole fraction of gas phase	[—]
Ω_a, Ω_b	= parameters in SRK equation	[—]

⟨Scripts⟩

l	= liquid phase
g	= gas phase
1	= 1,1-difluoroethane
2	= propylene
sat	= saturated
azeo	= azeotropy

Literature Cited

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