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Measurements of the Vapor–Liquid Coexistence Curve and the Critical Locus for Several Refrigerant Mixtures[1]

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Measurements of the vapor–liquid coexistence curve in the critical region for the systems of binary refrigerant mixture, i.e., Refrigerant 22 + Refrigerant 114 and Refrigerant 13B1 + Refrigerant 114, have been made by visual observation of the meniscus at the vapor–liquid interface within an optical cell. The experimental uncertainty of the temperature, density, and mass fraction is estimated within 15 mK, 0.5%, and 0.05%, respectively. The critical locus for these mixtures has been determined taking into consideration the disappearing meniscus level and the intensity of the critical opalescence. In accordance with the previous results of the Refrigerant 12 + Refrigerant 22 system, the coexistence curve for binary refrigerant mixtures is discussed. The composition dependence of the critical parameters for refrigerant mixtures is also discussed and compared with that of several predictive methods.

KEY WORDS: binary refrigerant mixture; critical parameter; critical locus; vapor–liquid coexistence curve.

1. INTRODUCTION

Nonazeotropic refrigerant mixtures have recently been of interest as prospective working fluids for refrigeration and heat pump cycles. Although the thermophysical properties of these refrigerant mixtures are of importance for evaluation of the cycle performance and for the design of the system, only very few experimental data are available. Particularly in the critical region, no investigation concerning the vapor–liquid coexistence curve and the critical locus has ever been reported.

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We have carried out investigations on the thermophysical properties of refrigerant mixtures systematically. Some of the results were published: the *PVTx* measurements of the R 12 (dichlorodifluoromethane:CCl_2F_2) + R 22 (chlorodifluoromethane:$CHClF_2$) system [1–3] and the R 22 + R 114 (1,2-dichlorotetrafluoroethane:$CClF_2CClF_2$) system [4], measurements of the vapor–liquid coexistence curve in the critical region and the critical locus for the R 12 + R 22 system [5], and an analysis of the application to the refrigeration cycle [6]. In this paper, measurements of the vapor–liquid coexistence curve in the critical region and the critical locus for the binary refrigerant mixture R 22 + R 114 system are reported, and some preliminary results of similar measurements for the R 13B1 (bromotrifluoromethane:$CBrF_3$) + R 114 system are also included. The composition dependence of the critical parameters for these refrigerant mixtures including the R 12 + R 22 system previously published [5] is also discussed and compared with that of several predictive methods.

2. EXPERIMENTAL

The vapor–liquid coexistence curve in the critical region for a certain composition of binary refrigerant mixtures was measured by observing the meniscus disappearance. The experimental apparatus used and procedures were described in detail in previous papers [5,7]. The apparatus was composed of an optical cell, an expansion vessel, and a supplying vessel. In the present study, a new optical cell made of 304 stainless steel was constructed. Silver packings between window and steel in place of Teflon packings were used for a seal, and the inner shape of the optical cell was modified from cylindrical to barrel-shaped in order to make it easy to observe the meniscus disappearance. The optical cell was disassembled twice during the present experiments due to experimental inconvenience. After each assemblage the inner volume of the optical cell was calibrated to be 13.461 ± 0.005 and $13.487 \pm 0.005\ cm^3$ by filling with water of known density values under room-temperature conditions. The expansion vessel and the supplying vessel were cylindrical and made of 304 stainless steel. Their inner volumes were 7.592 ± 0.005 and $77.052 \pm 0.005\ cm^3$, respectively.

In order to measure the saturation temperatures successively for a series of densities along the coexistence curve, we introduced an expansion technique [7] throughout the present measurements. The optical cell was connected with the expansion vessel to repeat the expansion procedures from the optical cell to the expansion vessel after the measurements of a saturation temperature. The supplying vessel was connected to both the optical cell and the expansion vessel, which allowed the sample in the supplying vessel to be supplied to the optical cell after the completion of a single series of expansion procedures. Careful attention was paid to the expansion procedure so as not to change the sample composition and also to homogenize the sample density after the expansion procedure.

The sample density in the optical cell can be calculated from the mass of the sample and the inner volumes of the three vessels used. With this method it is unavoidable that the experimental uncertainty in the density measurements becomes larger proportionally to the total number of expansion procedures. Therefore we restricted the number of expansion procedures to maintain the uncertainty of density measurements within 0.5%.

The prescribed quantity of each pure component, which was weighed in advance, was prepared separately and they were charged one by one into the supplying vessel immersed in the liquefied nitrogen. The mass fraction of the sample mixture thus provided was determined to be the ratio of the mass of each component to that of the mixture with an uncertainty of no greater than 0.05%.

The temperature measurements were conducted with a 25-Ω platinum resistance thermometer (Chino Model R800-1) calibrated with a precision of 5 mK on the IPTS-68 at the National Research Laboratory of Metrology, Ibaraki, Japan, with the aid of a thermometer bridge (either Tinsley Type 5840 or Shimadzu Type BD-100). The uncertainty in temperature measurements is estimated to be within 15 mK including the precision of the thermometer used, the fluctuation of the temperature controlled being ±10 mK, and an individual difference in the determination of the meniscus-disappearing temperature

3. RESULTS

3.1. Vapor–Liquid Coexistence Curve for Binary Refrigerant Mixtures

The experimental temperature–density data along the coexistence curve for four different compositions of 20, 30, 50, and 75 wt% R 22 for the R 22 + R 114 system are given in Table I and illustrated in Fig. 1, including both of pure components. Forty measurements for the R 22 + R 114 system cover the temperature range from 355 to 419 K and the density range from 280 to 896 $\mathrm{kg \cdot m^{-3}}$. Although the measurements for the R 13Bl + R 114 system are still underway, the results measured up to the present are illustrated in Fig. 2. The dashed line in Figs. 1 and 2 indicates the critical locus for respective mixtures. The measurements of the coexistence curve and the critical parameters of the pure components, i.e., R 22, R 13Bl, and R 114, were given in previous papers [5, 8, 9]. The purity of each component used was as follows: 99.99 wt% R 22, either 99.94 or 99.98 wt%

Table I. Experimental Data Along the Coexistence Curve for the R 22 + R 114 System

T (K)	ρ ($kg \cdot m^{-3}$)
20.00 wt% R 22	
403.52_8	318.9
404.73_7	362.3
405.23_7	391.3
404.66_9	449.3[a]
403.95_0	566.6[a]
402.75_8	611.6[a]
400.80_4	702.2
398.86_8	779.0
391.87_0	886.5
30.00 wt% R 22	
394.99_1	287.7
398.53_6	449.8[a]
398.13_1	501.5[a]
397.35_9	538.3[a]
397.21_4	550.5[a]
397.10_8	562.1[a]
397.02_8	572.8[a]
396.55_9	616.1[a]
393.81_0	703.6
391.41_0	784.6
384.60_7	896.2
50.00 wt% R 22	
385.74_0	279.3
386.03_1	288.9
386.64_3	316.8
387.44_2	361.2
387.66_0	389.1
387.70_2	451.8[a]
387.29_3	495.4[a]
386.56_6	543.9[a]
385.67_5	608.5
385.19_4	633.3
382.75_0	706.7
380.26_5	775.0
378.55_8	819.3
75.00 wt% R 22	
376.97_4	384.3
376.97_5	425.2[a]
376.20_0	541.4[a]
375.49_5	600.7
374.21_6	664.5
372.39_4	738.1
365.70_9	846.6

[a] Measured by observing the critical opalescence.

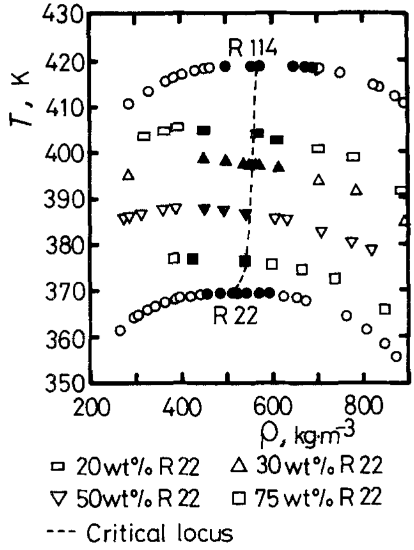

Fig. 1. Coexistence curves for the R 22 + R 114 system.

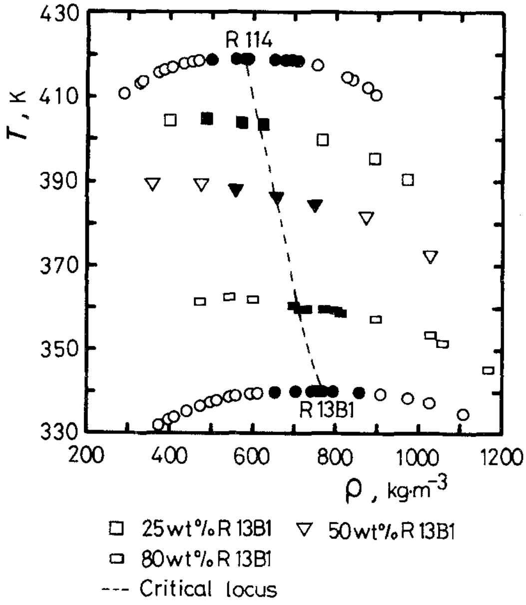

Fig. 2. Coexistence curves for the R 13B1 + R 114 system.

R 114, being an isometric blend of 95% $CClF_2CClF_2 + 5\% \ CCl_2FCF_3$, and either 99.965 or 99.990 wt% R 13B1.

The measurements at which the critical opalescence was observed are indicated by filled symbols in Figs. 1 and 2. The behavior of the meniscus and the intensity of the critical opalescence for the mixtures of the present systems were observed similarly as reported in previous papers [5, 8, 9] for the pure substances except those in the near-vicinity of the critical point. In this region, the critical opalescence at the vapor phase was observed as intensively as that at the liquid phase, while the meniscus ascended or descended very slightly. With the approach of the temperature to the critical temperature, the meniscus became indistinguishable at the center level of the optical cell and a fog band was formed. Then after the temperature was kept constant, as it was within a fluctuation of 5 mK for a period of 2 to 5 h, it was confirmed that this fog band had disappeared. Similar phenomena were observed in the case of R 114 [9].

3.2. Determination of the Critical Locus

We determined the critical temperature T_c and the critical density ρ_c of the respective compositions for the R 22 + R 114 system by analyzing the present measurements along the vapor–liquid coexistence curve, taking into consideration the disappearing meniscus level and the intensity of the critical opalescence. The critical pressure P_c of the respective compositions was determined graphically with the aid of the *PVTx* measurements by Hasegawa et al. [4] for the R 22 + R 114 system. The critical parameters thus obtained for the R 22 + R 114 system are given in Table II. The mass

Table II. Critical Parameters for the R 22 + R 114 System

Composition of R 22				
w_1 (wt%)	x_1 (mol%)	T_c (K)	ρ_c (kg · m^{-3})	P_c (MPa)
0[a]	0	418.78 ± 0.02	576 ± 3	3.252 ± 0.004
20.00	33.07	403.89 ± 0.10	563 ± 10	4.09 ± 0.03
30.00	45.86	397.15 ± 0.02	558 ± 5	4.26 ± 0.03
50.00	66.41	386.52 ± 0.05	550 ± 10	4.62 ± 0.03
75.00	85.57	376.16 ± 0.03	545 ± 5	4.93 ± 0.03
100[b]	100	369.32 ± 0.01	515 ± 3	4.990 ± 0.005

[a] From Ref. 9.
[b] From Ref. 5.

fraction of respective compositions for the mixture was converted into the mole fraction by using the molar mass of 86.469 and 170.922 $g \cdot mol^{-1}$ for R 22 and R 114, respectively. The results of the critical parameters for the R 13Bl + R 114 system will be published later.

4. DISCUSSION

4.1. Vapor–Liquid Coexistence Curve

Although the shape of the vapor–liquid coexistence curves for respective compositions for the R 12 + R 22 system was similar to that for pure components, the shape of the vapor–liquid coexistence curves of both the R 22 + R 114 system and the R 13Bl + R 114 system were different from those of pure components as shown in Figs. 1 and 2. The density of the maximum temperature along the coexistence curve, the so-called "maxcondentherm point" or "cricondentherm point," shifts from the critical density of respective compositions to the lower density by about 150 to 200 $kg \cdot m^{-3}$ for the mixtures of the R 22 + R 114 system. The temperatures at the maxcondentherm point for the R 22 + R 114 system are higher by about 0.8 to 1.5 K than the critical temperature of the respective compositions determined by visual observations, whereas these temperature differences for the R 12 + R 22 system do not exceed 0.2 K. Similar temperature differences, however, are expected to become significant for the R 13Bl + R 114 system. These observations support the fact that the shape of the vapor–liquid coexistence curve depends heavily upon the magnitude of the critical temperature difference between two pure components.

4.2. Critical Locus

The critical locus for the R 22 + R 114 system and the R 13Bl + R 114 system is illustrated on a temperature–density plane in Fig. 3 together with the critical locus for the R 12 + R 22 system and the coexistence curve for four pure refrigerants, i.e., R 12, R 22, R 13Bl, and R 114, which have been published elsewhere [5, 8, 9]. On the temperature–density plane in Fig. 3, the critical locus of the R 13Bl + R 114 system is expected to be linear. The critical locus of the R 22 + R 114 system is almost linear but it seems to bend sharply at temperatures close to the critical point of pure component of R 22, as well as that for the R 12 + R 22 system. These behaviors of the critical locus for the binary refrigerant mixtures are considered to be influenced considerably by the polarity of pure components. All of the halogenated hydrocarbon refrigerants of present interest are polar substances and their values of

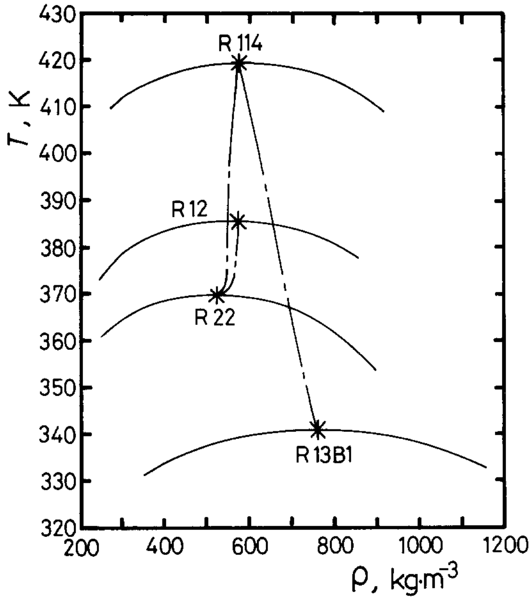

Fig. 3. Critical locus for binary refrigerant mixtures.

dipole moment are 0.51 D for R 12, 1.42 D for R 22, 0.65 D for R 13Bl, and 0.5 D for R 114 [10]. It is noted that the dipole moment for R 22 is about three times greater than that for three other refrigerants, and this fact suggests that the critical locus of binary refrigerant mixtures including R 22 bends sharply at the rich compositions of R 22 due to strong polarity.

We have already discussed the critical locus for the R 12 + R 22 system [5] with the predictive approaches by Li [11], Chueh and Prausnitz [12], and Kreglewski and Kay [13], which are recommended by Reid et al. [14]. In the present study, the approach based on the Soave–Redlich–Kwong equation of state (SRK equation) [15] as well as three previous approaches are discussed for the R 12 + R 22 system and the R 22 + R 114 system. The binary interaction parameters in the SRK equation, k_{12}, for the R 12 + R 22 system and the R 22 + R 114 system, were determined to minimize the average deviation for respective compositions on the basis of the present results for the critical temperature.

The composition dependence of the critical temperature for the R 22 + R 114 system is shown in Fig. 4 in accordance with the results of the predictive method by Li, by Chueh and Prausnitz, and by the SRK equation. With respect to the R 12 + R 22 system reported previously [5], the results of two predictive methods, by Li and by Chueh and Prausnitz, are much higher than the experimental data, by about 0.5 to 1%, and can-

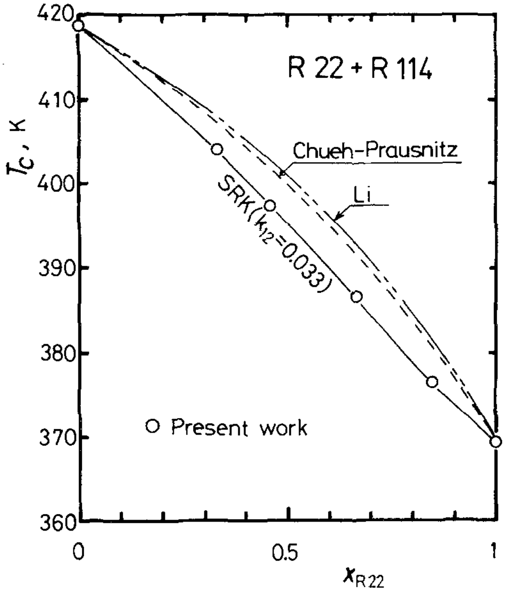

Fig. 4. Composition dependence of the critical temperature for the R 22 + R 114 system.

not predict the concave behavior of this critical locus. However, the critical temperatures calculated from the SRK equation, with $k_{12} = 0.035$ fitting in with the experimental data, exhibit the average deviation of 0.024%. As shown in Fig. 4, although the critical temperatures due to the two predictive methods by Li and by Chueh and Prausnitz for the R 22 + R 114 system are much higher than the experimental data, by about 1 to 2.5%; the average deviation of the predictive results by the SRK equation at $k_{12} = 0.033$ from the experimental data is 0.061%. The composition dependence of the critical pressure for the R 22 + R 114 system is shown in Fig. 5, including the results of the predictive method by Kreglewski–Kay and by the SRK equation. In order to calculate the critical pressure by the SRK equation, the value of the binary interaction parameter, k_{12}, determined from the critical temperature is adopted. The result of the predictive method by Kreglewski–Kay for the R 12 + R 22 system is much lower, by about 1 to 2%, while for the R 22 + R 114 system these are in good agreement within the estimated uncertainty. From the results of the predictive method by the SRK equation in Fig. 5, it is clear that the optimum value of the binary interaction parameter, k_{12}, determined from the critical temperature is not suitable for the predicted critical pressure for the same mixture. This fact is

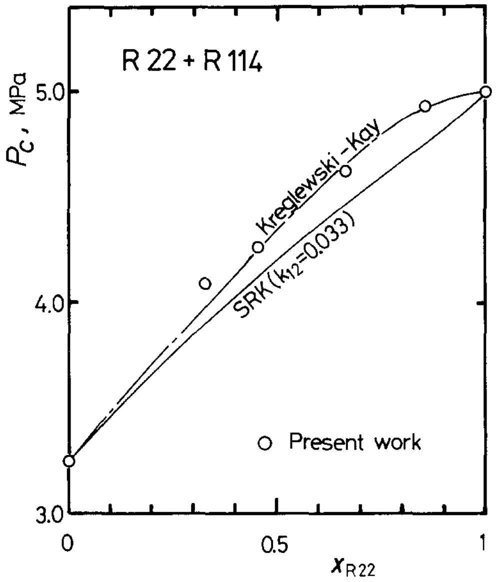

Fig. 5. Composition dependence of the critical pressure for the R 22 + R 114 system.

also valid for the critical pressure for the R 12 + R 22 system. The composition dependence of the critical molar volume for the R 22 + R 114 system is shown in Fig. 6 together with the results of the predictive method by Chueh and Prausnitz and by the SRK equation. The value of the binary interaction parameters, k_{12}, used by the prediction of the critical temperature and the critical pressure is also adopted. The results of the predictive method by Chueh and Prausnitz for the R 12 + R 22 system are in good agreement with the experimental data within the estimated uncertainty. Those for the R 22 + R 114 system, however, are much lower than the experimental data, by about 5 to 15%. With the predictive method by the SRK equation, the results not only for the R 22 + R 114 system in Fig. 6 but also for the R 12 + R 22 system do not reproduce the experimental data, and even the critical molar volume for pure components can hardly be calculated.

By examining the results predicted by the SRK equation, it becomes clear that it is essential to introduce the interaction parameter, k_{12}, even in the prediction of the critical locus. However, it was impossible to reproduce all of the critical parameters with a high accuracy by applying the common k_{12} value. It seems fair to add that it is essential to have the optimum k_{12} value for the prediction of the critical locus for arbitrary binary mixtures with the aid of a so-called two-constant equation of state such as the

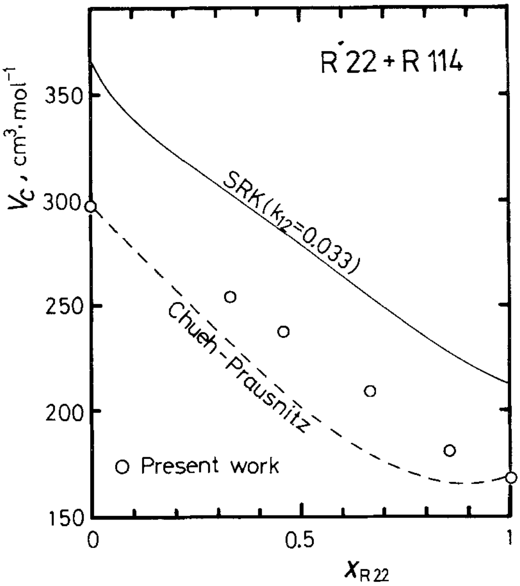

Fig. 6. Composition dependence of the critical molar volume for the R 22 + R 114 system.

SRK equation. However, there exist a few high quality correlations with respect to k_{12} effective to predict the critical locus; no single correlation has ever been reported especially for the binary mixtures including polar components, such as those of the present interest.

Hence, it is concluded that the application of the two-constant equation of state to the prediction of the critical locus for arbitrary binary-mixture systems requires somewhat elaborate computations but results in rather less-productive conclusions. Instead, the present authors recommend utilizing any simple empirical methods of prediction after the considerable improvements in the existing methods such as those by Li [11] and by Chueh and Prausnitz [12]. In this connection, as discussed in Section 4.1, it seems essential to take into consideration the effects of polarity to a satisfactory extent for our further developments in improved predictive methods with respect to the critical locus.

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