

## **Current Thermophysical Properties Research on Refrigerant Mixtures in Japan**

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This paper reviews the thermophysical properties of nonazeotropic refrigerant blends (NARBs), which are prospective working fluids, especially for advanced heat pump systems as well as for other industrial applications such as ultra-low-temperature freezers for medical use, domestic air-conditioners, etc. After a brief introduction on the thermodynamic behavior of NARBs, the current state of thermophysical-properties research for NARBs, which are possible candidates for CFC alternatives, is reviewed. The thermophysical properties discussed in this paper include not only thermodynamic properties such as  $PVT_x$  properties, vapor-liquid equilibria, critical parameters, etc., but also transport properties such as viscosity and thermal conductivity. Emphasis is placed on the most recent results resulting from an extensive research project partially supported by the Japanese Association of Refrigeration (JAR) on the occasion of its 60th foundation anniversary, celebrated in 1985. In view of the urgent demand to accumulate information on various thermophysical properties of CFC alternatives including R134a and R123, some of our current activities in Japan are presented. A task force to provide a set of reliable thermophysical properties for engineering use of CFC alternatives has been organized with partial support from the Ministry of International Trade and Industry, Japan.

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**KEY WORDS:** CFC alternatives; nonazeotropic refrigerant blends (NARBs); refrigerant mixtures; refrigerants.

### **1. INTRODUCTION**

From a global perspective, it is needless to stress the importance of efficient use of energy in terms of higher energy productivity through energy conservation measures.

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Increasing attention to the R&D of advanced heat pump systems is exactly reflecting these demands, since they are able to promote the efficient use of energy by utilizing thermal energy with moderate and/or lower temperature levels and by upgrading the temperature suitable to various industrial and domestic applications. Among the possible technical approaches toward the R&D of advanced heat pump systems, it is necessary to select the optimum working fluid for the system concerned. The candidates in the case of advanced vapor-compression heat pump systems are nonazeotropic refrigerant blends (NARBs), which may provide some benefits in terms of energy conservation, enhanced thermal lift capability, and performance modulating potential. In addition, it is also noteworthy to mention that NARBs may play an important role as possible ozone benign CFC alternatives.



This paper attempts to present a survey of ongoing research on thermophysical properties of NARBs as well as CFC alternatives in Japan. The discussion covers not only the thermodynamic properties but also the basic transport properties.


## **2. THERMOPHYSICAL PROPERTIES OF NARBs**


### **2.1. General Background**

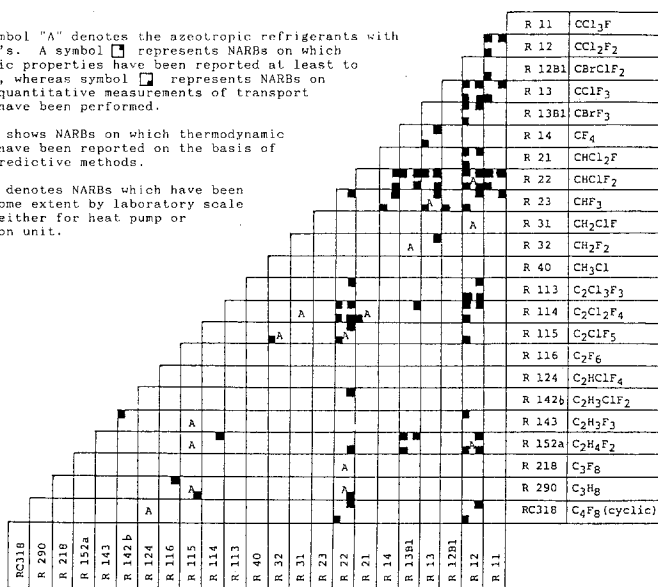
There is no doubt that one should have a set of reliable thermophysical property values of refrigerants in any stage of engineering applications: planning, designing, operation and control, testing, and performance evaluation of advanced vapor-compression heat pump systems.

The available information on thermophysical properties of NARBs is very much limited [1-4] in comparison with those of single-component refrigerants, due mainly to the fact that the precise measurements of thermophysical properties for NARBs are so elaborate and are accompanied by many difficulties in conducting extensive measurements specifically for covering a wide variety of compositions. Figure 1 summarizes the current state of the art with respect to the available information on the thermophysical properties of NARBs, even including information about laboratory-scale rig tests for heat pumps using NARBs that have been investigated [4]. It is interesting to note that the studied and/or proposed blends include the most popular refrigerants such as R12, R22, R13B1, and R114 as their pure components, although they mostly belong to a group of fully halogenated fluorocarbons whose use is questioned because of their long life in the atmosphere as well as their considerable ozone depletion potential in the stratosphere. However, it is also noteworthy to point out that there exist still more possibilities to examine new blends available for

NOTE : A symbol "A" denotes the azeotropic refrigerants with numbers 500's. A symbol  represents NARBs on which thermodynamic properties have been reported at least to some extent, whereas symbol  represents NARBs on which some quantitative measurements of transport properties have been performed.

A symbol  shows NARBs on which thermodynamic properties have been reported on the basis of available predictive methods.

A symbol  denotes NARBs which have been tested to some extent by laboratory scale ring tests either for heat pump or refrigeration unit.



**Fig. 1.** Mapping of NARBs currently concerned and availability of their thermophysical property data.

safe and advanced heat pump technology, since we can find many open spaces in the mapping shown in Fig. 1. This fact suggests that we do need to accumulate further reliable data for the essential thermophysical properties of new binary blends of stratospherically safe refrigerants, to find any NARBs or azeotropes for the conventional single-component refrigerants.

Although the thermophysical properties of NARBs have not been investigated to a satisfactory extent, the availability of thermodynamic properties is much better than that of transport properties in both quantity and quality. However, it seems to the present author inevitable to produce more reliable sets of directly observed data for thermodynamic properties such as vapor-liquid equilibria (VLE),  $PVT_x$  properties, and isobaric specific heat capacity. The same is also true and urgent for transport properties such as viscosity and thermal conductivity, since their composition dependence over a wide range of temperature and pressure has not been investigated for most of the NARBs surveyed in Fig. 1.

Having surveyed this situation, the Japanese Association of Refrigeration (JAR) has organized a task force composed of several experts from different institutions in Japan to investigate the thermophysical properties more systematically and extensively. This research program has been initiated in 1985 on the occasion of JAR's 60th anniversary of foundation

within a special R&D Program for Heat Pump Technology [5]. The Task Force for Thermophysical Properties of NARBs, convened by the present author, has been organized to improve our knowledge of the thermophysical properties with various approaches: precise measurements of  $PVT_x$  properties, vapor-liquid coexistence curves, critical parameters, viscosity, thermal conductivity, and solubility into refrigeration oils (the latter property not for NARBs but for conventional pure refrigerants), in addition to some analytical studies of estimating thermodynamic properties of NARBs.

## 2.2. Thermodynamic Properties

Our research group at Keio University, Yokohama, initiated an extensive research program on the experimental studies of thermodynamic properties of NARBs in 1977 on the basis of our previous contributions in measuring various thermodynamic properties of different kinds of single-component halogenated hydrocarbons [1, 3]. At the very beginning of the program, we found that some earlier investigations in this field were more or less restricted to VLE measurements such as those reported by Kriebel and Löffler [6] for the R11 + R13 system, by Piacentini and Stein [7] for the R14 + R23 system, by Kraus et al. [8] for the R12 + R113 and R22 + R114 systems, by Mollerup and Fredenslund [9] for the R12 + R13 system, by Kruse and Holdak-Jansen [10] for the R11 + R12 system, by Jakobs [11] for the R12 + R114 system, and by Connon and Drew [12] for the R13B1 + R152a system, although some of them have covered  $PVT_x$  property measurements to some extent. Therefore, we concluded that more extensive measurements of the  $PVT_x$  properties over a wide range of temperature, pressure, density, and composition are definitely needed.

### 2.2.1. $PVT_x$ and BPC/DPC Measurements

The experimental measurements of  $PVT_x$  properties as well as boiling-point curve (BPC)/dew-point curve (DPC) determinations have been performed using a constant-volume method coupled with isothermal expansion procedures of the sample with the composition being kept unchanged. The NARBs we have completed up to the present are five binary systems: R12 + R22 [13–16], R22 + R114 [17], R13B1 + R114 [18], R152a + R114 [19], and R115 + R114 [20], respectively. As the sixth blend, we are currently measuring the R142b + R22 system, which has been proposed as one of the most promising NARBs for substituting the conventional refrigerant, R12.

Table I summarizes these measurements mentioned above and the

Table I. PVTx and VLE Measured Data at Keio University, Yokohama

NARBs	No. of data		Composition, x		Temperature, T		Pressure, P		Density, $\rho$	
	PVTx	VLE	$x_1$ (%)	$\Delta x$ (%)	Range (K)	$\Delta T$ (mK)	Range (MPa)	$\Delta P$ (kPa)	Range ( $\text{kg} \cdot \text{m}^{-3}$ )	$\Delta \rho$ (%)
R12 + R22	343	290	100, 90, 80, 70, 50, 25, 0	0.05	293-413	10	0.5-9.7	2.2	115-1150	0.1
R22 + R114	207	180	100, 75, 50, 30, 20, 0	0.12	283-443	10	0.1-9.7	2.0	94-1104	0.05
R13B1 + R114	275	222	100, 80, 70, 50, 25	0.10	303-443	8	0.5-10	2.0	150-1200	0.15
R152a + R114	328	316	100, 90, 80, 50, 20, 0	0.10	303-443	8	0.4-9.7	3.0	160-1300	0.16
R115 + R114	311	231	100, 75, 50, 25	0.05	302-413	8	0.4-9.8	2.2	153-1387	0.10

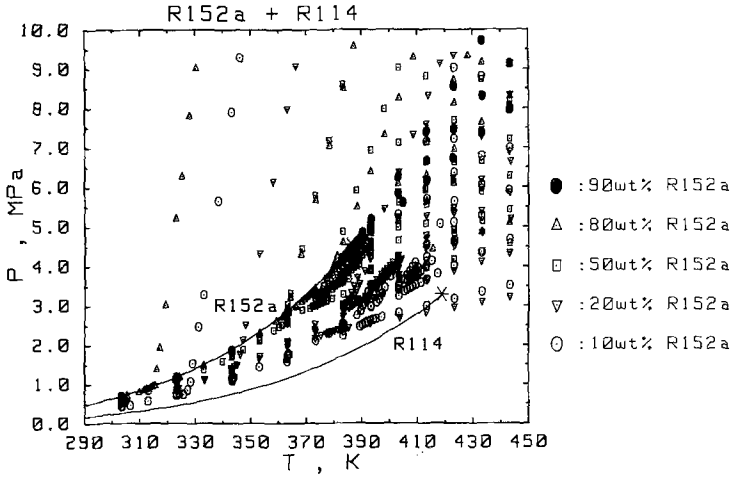


Fig. 2. Distribution of measured  $PVTx$  property data for the R152a + R114 system.

number of observed data points, range of composition, temperature, pressure, and density together with their respective experimental uncertainties. As a typical example of the data distribution observed throughout our  $PVTx$  property measurements, a set of 644 data for R152a + R114 blends is shown in Fig. 2. It should be noticed that  $PVTx$  property measurements are elaborate and pains-taking experiments, since the data shown in Fig. 2 are almost equivalent to cover the  $PVT$  property measurements for six

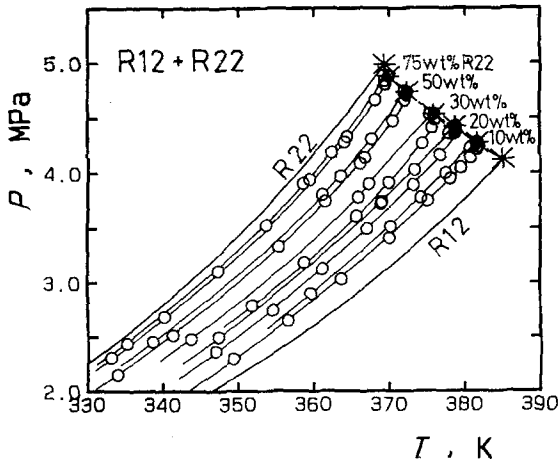


Fig. 3. Measured bubble- and dew-point curves for the R12 + R22 system.

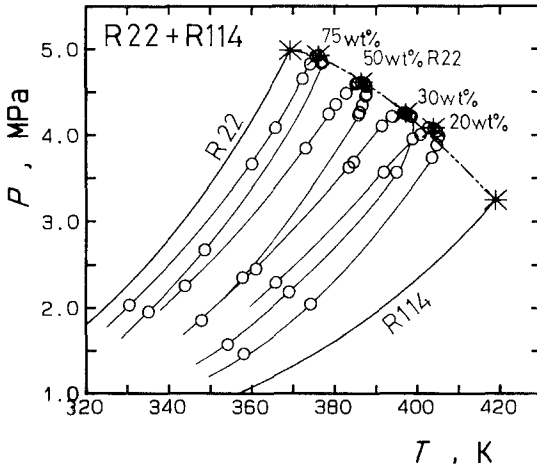


Fig. 4. Measured bubble- and dew-point curves for the R22 + R114 system.

different single-component refrigerants in the same wide range of state parameters.

Having analyzed these  $PVT_x$  property data graphically, we have determined bubble and dew points for the respective compositions by finding the breaking points of each isochore plotted on a pressure vs temperature graph. Regarding several isochores near the critical point, however, it is usually difficult to identify the breaking point along each

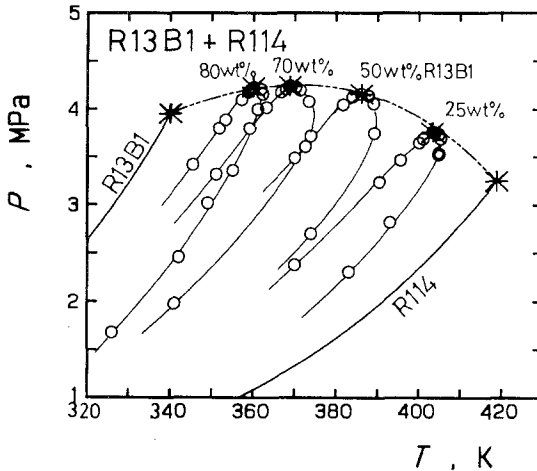


Fig. 5. Measured bubble- and dew-point curves for the R13B1 + R114 system.

isochore in this manner, so that we had to determine it with the aid of other data on the vapor-liquid coexistence curve as discussed below. The final BPC/DPC data thus determined are shown in Figs. 3-7 together with the critical loci for five different NARBs measured. By examining these BPC/DPC data carefully, it becomes clear that the phase-boundary curves consisting of BPC and DPC differ significantly in their shapes. Namely, the spread of envelope of the phase-boundary curve, i.e., the pressure difference between the bubble and the dew point at a specified temperature and composition, becomes smaller, for example, in the case of the R12 + R22 system, whereas it is much larger for other blends such as the R13B1 + R114 system. Such a difference is closely related to the differences in both the critical temperature and the critical pressure of each pure component. Table II summarizes the reliable sets of the critical parameters recently determined from our own measurements [20, 22-25]. Table III, on the other hand, shows the differences in the critical temperature, pressure, and density of each pure component for five different NARBs mentioned above. For reference, the reported information about dipole moments of respective pure refrigerants is also given in the parentheses (in Debyes) in Table III.

By comparing the difference in the critical temperatures of two components given in Table III with the spread of the phase-boundary curves for each NARB shown in Figs. 3-7, it may be possible to suggest that the

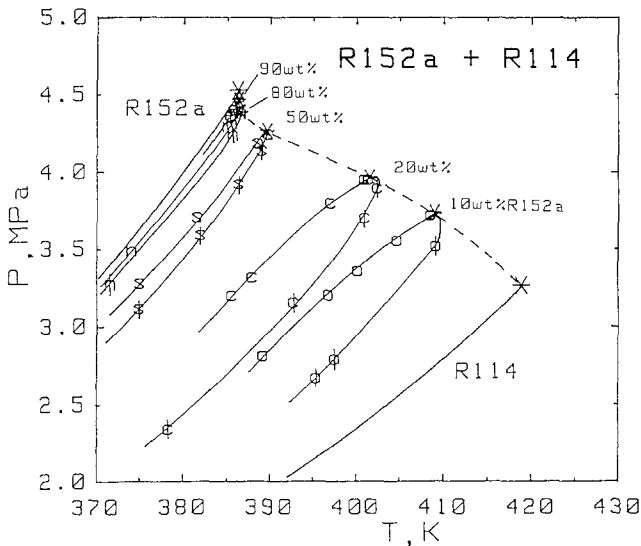


Fig. 6. Measured bubble- and dew-point curves for the R152a + R114 system.



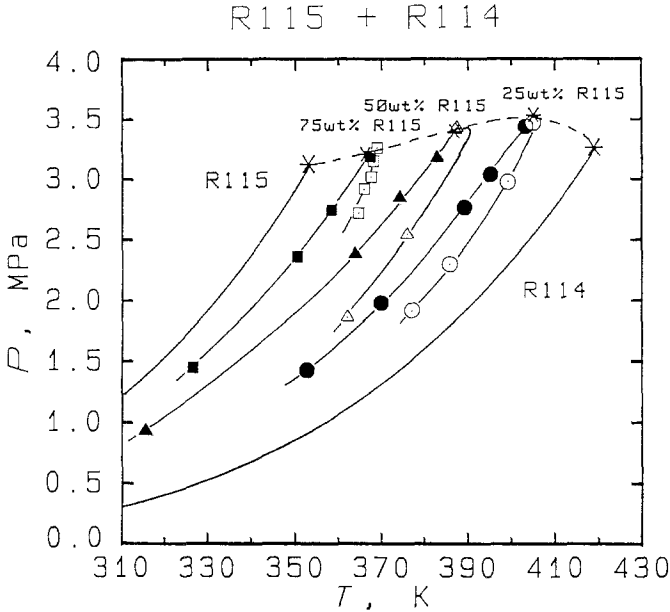


Fig. 7. Measured bubble- and dew-point curves for the R115+R114 system.

maximum spread is observed for the R13B1 + R114 system, which exhibits the largest difference in the critical temperature, while the minimum spread corresponds to the R12 + R22 system, with the smallest difference in the critical temperature. However, such a relation is not always applicable to other NARBs we have studied, since the blends consisting of refrigerants with rather greater dipole moments as their components, such as in the case of the R152a + R114 system in Fig. 6 as well as the R22 + R114 system in Fig. 4, the difference in the critical temperatures does not directly relate to the width of spread. This fact reflects that the spread of the phase-boundary

Table II. Critical Parameters for Several Refrigerants

	$T_c$ (K)	$P_c$ (MPa)	$\rho_c$ ( $\text{kg} \cdot \text{m}^{-3}$ )	Ref. No.
R12	$385.01 \pm 0.01$	$4.129 \pm 0.008$	$568 \pm 3$	22
R22	$369.32 \pm 0.01$	$4.990 \pm 0.005$	$515 \pm 3$	22
R13B1	$340.08 \pm 0.01$	$3.956 \pm 0.002$	$764 \pm 3$	23
R114	$418.78 \pm 0.02$	$3.252 \pm 0.004$	$576 \pm 3$	24
R115	$352.945 \pm 0.010$	$3.118 \pm 0.002$	$604 \pm 3$	25
R152a	$386.44 \pm 0.01$	$4.5198 \pm 0.0010$	$368 \pm 2$	20

**Table III.** Differences in Critical Parameter Values of Components for NARBs Studied

	$ \Delta T_c $ (K)	$ \Delta P_c $ (MPa)	$ \Delta \rho_c $ ( $\text{kg} \cdot \text{m}^{-3}$ )	$ \Delta \mu $ (D)
R12 + R22 (0.51) <sup>a</sup> (1.42)	15.69	0.861	53	0.91
R22 + R114 (1.42) (0.50)	50.46	1.738	61	0.92
R13B1 + R114 (0.65) (0.50)	78.70	0.704	188	0.15
R152a + R114 (2.27) (0.50)	32.34	1.267 <sub>8</sub>	208	1.77
R115 + R114 (0.52) (0.50)	66.83 <sub>5</sub>	0.134	28	0.02

<sup>a</sup> Figures in the parentheses are values of the dipole moment in Debyes.

envelope for NARBs depends on the difference in the critical temperature to some extent, but it is also strongly dependent on the difference in dipole moments of the pure components, especially when the refrigerant with stronger polarity, such as R152a and R22, is blended for the mixture. It may also be interesting to examine the size of the molecule of the pure component in relation to the dipole moments for our better understanding of the behavior discussed above. Since the spread of the phase-boundary curves for NARBs is closely related to the estimation of heat pump performance as discussed previously [1, 3, 4], it seems essential to examine in more detail this behavior of VLE data, so as to find any useful method of approach toward the optimum selection of NARBs for advanced heat pump applications in view of additional information on the molecular structure of the refrigerant components.

It is also interesting to note that the BPC/DPC envelope with an equi-mass composition locates almost in the center of two vapor-pressure curves of the respective components in the case of NARBs with smaller differences in dipole moment. This fact may be observed in the case of the R13B1 + R114 system (see Fig. 5) as well as the R115 + R114 system (see Fig. 7), which have a difference in dipole moment of 0.15 and 0.02, respectively, as shown in Table III. It should also be noted that this equimass envelope shifts significantly toward the vapor-pressure curve of the pure component with a larger dipole moment as typically shown in the case of the R152a + R114, R12 + R22, and R22 + R114 blends (see Figs. 3, 4, and 6). This fact suggests again that the strong polarity of the refrigerant com-

ponents play an important role in predicting such a thermodynamic behavior of the VLE-data.

Regarding the critical locus of NARBs, it is found that the R22 + R114 and the R13B1 + R114 systems exhibit convex curves, while the R12 + R22 blends shows an almost linear but slightly convex trend. On the other hand, two other NARBs, the R152a + R114 and the R115 + R114 systems, behave rather differently. For example, in the case of the R152a + R114 system in Fig. 6, the critical locus shows a steep decrease in pressure, especially for R152a-rich compositions, although it behaves with moderate convex trend in general. Figure 8 summarizes these critical loci plotted on a common pressure vs temperature plane. It is interesting to note that the critical pressure of the R12 + R22, R22 + R114, and R152a + R114 blends decrease almost monotonically with increasing temperature, whereas those of the R13B1 + R114 and R115 + R114 blends deviate considerably from the tie line between the critical points of pure components.

### 2.2.2. Critical Parameters and Coexistence Curves

The second program we have continued at Keio University is the measurement of the critical parameters as well as of the vapor-liquid coexistence curves near the critical point of NARBs. The principle of the measurements is the direct observation of the vapor-liquid meniscus disappearance. In other words, we are able to measure the saturated vapor and

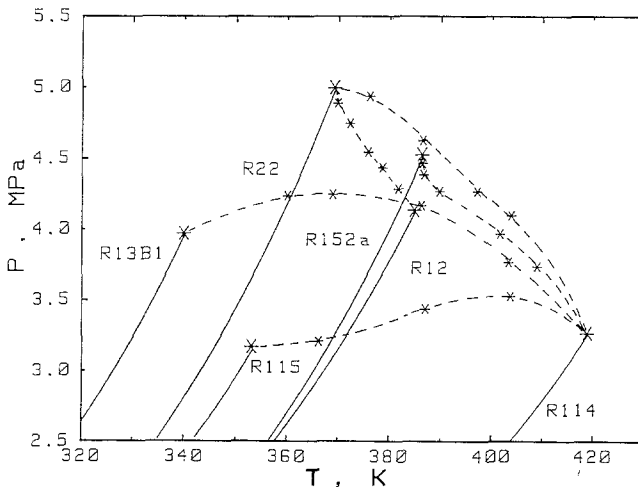


Fig. 8. Critical loci of NARBs shown on a pressure vs temperature diagram.

liquid densities of the sample mixture by knowing the inner volumes of an optical cell with synthetic sapphire windows and of supplementary expansion vessels and the mass of the sample confined. The measurements are always conducted to determine the temperature, when the meniscus disappears with the aid of careful observation of the meniscus disappearing level within the optical cell as well as of the critical opalescence. We have measured exactly the same blends under this program as those used for  $PVT_x$  property measurements. Most of our experimental determinations of the critical temperature, critical density, and composition have been performed with estimated uncertainties of 10 mK, 2 or  $3 \text{ kg} \cdot \text{m}^{-3}$ , and 0.05%, respectively. The critical pressure, however, has been determined analytically on the basis of the developed vapor-pressure correlation for pure refrigerants as well as of the graphical interpretation of  $PVT_x$  property data in the light of directly observed data for the critical temperature and density, since the present measurements have been always conducted at the same compositions as those for  $PVT_x$  property measurements. Figures 9–12 show the results obtained for the vapor–liquid coexistence curves for the NARBs studied [22, 26–28]. The filled symbols in the vicinity of the respective critical points denote data points which have been deduced from the observed critical opalescence, while the dashed curves are the critical loci connecting the respective critical points denoted by the

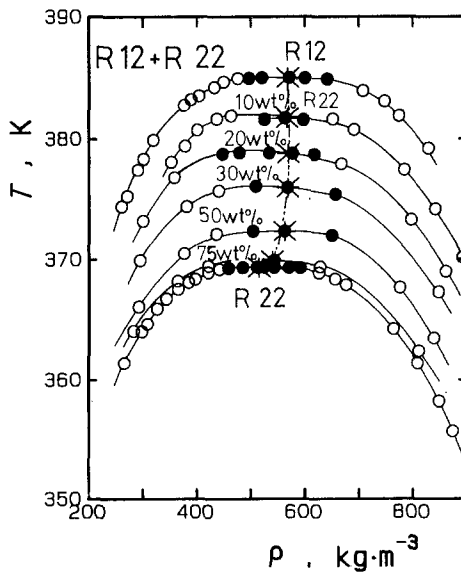


Fig. 9. Measured vapor–liquid coexistence curves for the R12 + R22 system.

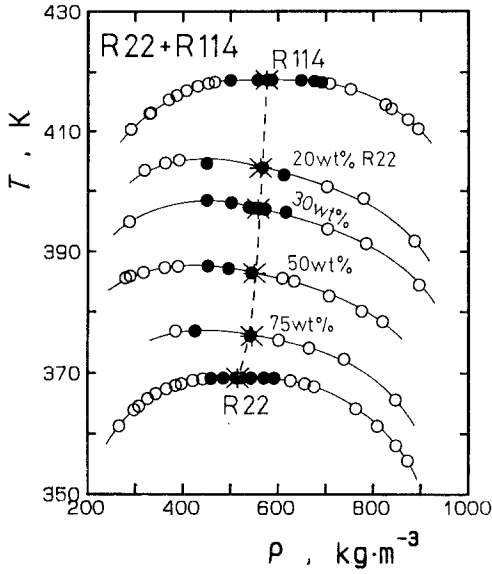


Fig. 10. Measured vapor-liquid coexistence curves for the R22 + R114 system.

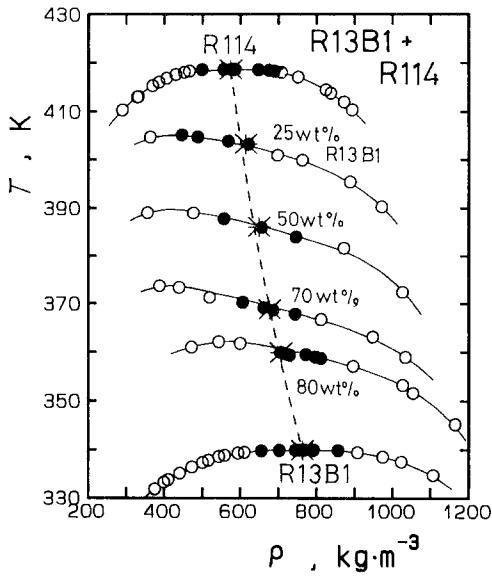


Fig. 11. Measured vapor-liquid coexistence curves for the R13B1 + R114 system.

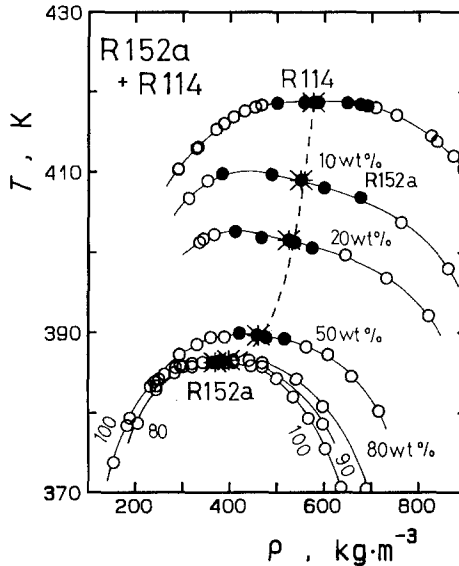


Fig. 12. Measured vapor-liquid coexistence curves for the R152a + R114 system.

symbol \*. Another, fifth blend of the R115 + R114 system is currently under investigation and the results will be reported elsewhere [25].

Figure 9 shows the results for the R12 + R22 system [22], which behaves almost similarly to the coexistence curves of both pure components. However, another three NARBs, i.e., the R22 + R114 system [26], the R13B1 + R114 system [27], and the R152a + R114 system [28], exhibit somewhat different behavior from the corresponding coexistence curves of the pure components, as can be clearly seen from Figs. 10–12. It is interesting to note that the vapor-liquid coexisting temperatures at the saturated vapor of these three binary mixtures are always higher than the critical temperature of the respective mixtures, whenever significant critical opalescence has been observed. It is also noteworthy that the critical locus plotted on a temperature vs density plane behaves differently in each binary mixture. One rare exception with a nearly straight line has been observed for the critical locus of the R13B1 + R114 system, while other critical loci bend with considerable sharpness near the critical point of the polar component of the blends, e.g., the R152a + R114 system in Fig. 12. This fact implies that the strong polarity of refrigerants such as R152a and R22 plays an essential role in exhibiting such an interesting behavior, as discussed already in conjunction with  $PVT_x$  property measurements.

It should be noted that the existence of the maxcondentherm points in

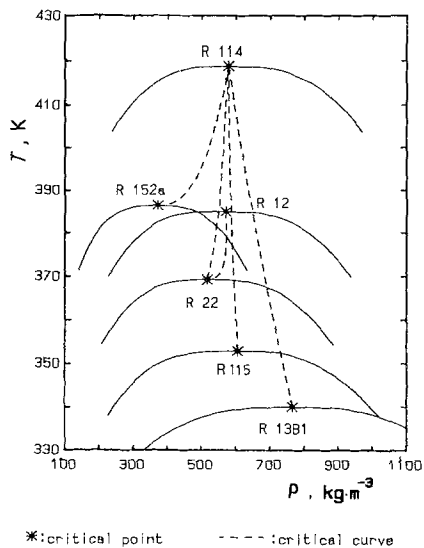


Fig. 13. Critical loci of NARBs shown on a temperature vs density diagram.

a smaller density region for NARBs is clearly observed again for the blends which have shown somewhat considerable spreads in their phase-boundary envelopes, as seen for the R13B1 + R114 system (see Figs. 11 and 5). Figure 13 summarizes the critical loci of five NARBs measured including the unpublished results for the R115 + R114 system [25]. Some further analysis of these results may give us additional knowledge how to predict any typical behavior of the vapor-liquid coexistence curves for NARBs in terms of their molecular structure.

### 2.3. Transport Properties

It is our common understanding that the transport properties of NARBs, especially viscosity and thermal conductivity, are essential in the analysis of heat and mass transfer processes within the heat exchangers, i.e., evaporator and condenser, of the advanced heat pump systems. In spite of their importance, however, available information on the transport properties of NARBs is still very much limited in quantity and quality in comparison with that on the thermodynamic properties.

Among a few earlier investigations on thermal conductivity of NARBs, there exists a contribution by Puranasamriddhi [29], who measured the R12 + R22 system by a stationary hot-wire method. Unfortunately,

however, the reported results for three different compositions are given only in graphical form together with a proposed correlation within the limited temperature range of 255–293 K under atmospheric pressure.

Earlier investigations on the viscosity include the works by Srichand et al. [30], who have reported viscosity for the R12 + R22 system measured by an oscillating disk viscometer for temperatures from 299 to 300 K and at 104 kPa. More recent viscosity measurements for the R12 + R113 and R22 + R114 systems have been conducted by Heide [31], who used a falling-ball viscometer. Unfortunately again, the results are merely presented graphically.

Having surveyed such a rather unsatisfactory situation for transport properties, two active members of our task force at the JAR have initiated extensive research programs at two institutions in Japan: Makita and his colleagues at Kobe University in Kobe and Takahashi and his co-workers at Tohoku University in Sendai. Makita et al. are currently measuring both the thermal conductivity and the viscosity of NARBs extensively, while Takahashi et al. are also continuing other precise measurements of the viscosity with oscillating viscometry.

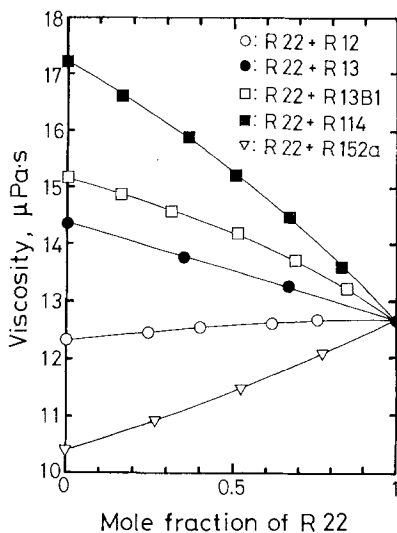
Concerning thermal conductivity measurements, Makita et al. are using a coaxial cylinder method on a relative basis and the experimental results on the R22 + R152a blends for temperatures of 298–498 K and pressures up to 1.5 MPa as well as those on the R22 + R14 system for temperatures of 323–348 K and pressures up to 2.5 MPa have been reported [32]. They have estimated the experimental uncertainty in thermal conductivity as less than 2.0%. It is noted from their measurements that the thermal conductivity at each composition increases with increasing pressure, while at constant temperature it decreases almost linearly with increasing mole fraction of component R22. Their results on the composition dependence of the thermal conductivity of the R22 + R14 system under higher pressures have been compared with available methods of prediction: the Hirschfelder-Eucken equation and Stiel-Thodos equation. They have also commented on the predictive methods for thermal conductivity of NARBs at both the normal pressure and higher pressures and they have proposed a set of the optimum combination factors to be applied to Wassiljewa's theory. The present author has been informed that they are continuing similar measurements for the R22 + R23 and R22 + R13 systems.

Another program on viscometry of NARBs is also in progress at Kobe University. Makita and his colleagues are using a rolling-ball viscometer to measure the gaseous viscosity of binary mixtures at the normal pressure for several compositions and wide range of temperatures. Nagaoka et al. [33] have reported data for eight different gaseous blends including the R290

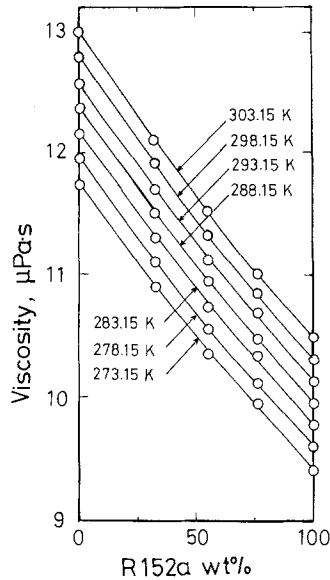


(propane) + R22, R290 + R115, R290 + R502 (strictly speaking, this is a ternary mixture), R22 + R12, R22 + R13, R22 + R13B1, R22 + R14, and R22 + R152a systems. The measurements have been performed for temperatures of 298–343 K at atmospheric pressure and they have claimed an experimental uncertainty of less than 1.0%. It is interesting to note that the viscosity of all the gaseous mixtures at constant temperature varies almost linearly with composition as typically shown in Fig. 14. The measured data have been correlated with an empirical Sutherland correlation (solid curves in Fig. 14) with a mean deviation of 0.36%, while the Chapman-Enskog theory reproduces the data with a mean deviation within 1% except for the R290 + R502 blends, a ternary mixture.

On the other hand, Takahashi et al. [34] have reported 250 measured data for the viscosity of the R22 + R152a system for the range of temperatures 273–303 K and pressures up to 0.7 MPa. The measurements have been performed with a Maxwell-type disk viscometer, while they have also reported the density of blends exactly at the same condition measured by a high-pressure pipette method. The experimental uncertainties claimed are 0.3% in viscosity and 0.12% in density, respectively. They have obtained measurements for five compositions including two pure components. One typical example of their experimental results for the atmospheric viscosity values is shown in Fig. 15. It has been discussed in their original paper that



**Fig. 14.** Composition dependence of viscosity for NARBs including R22 at 298.15 K.



**Fig. 15.** Composition dependence of viscosity for the R152a + R22 system at atmospheric pressure.

the atmospheric viscosity could be well predicted with the Sutherland-Thiessen equation associated with the coefficients approximated by Brokaw's method. An experimental correlation of the viscosity has been developed also as a function of composition, temperature, and pressure and they have tabulated a set of smoothed viscosity values at nominal temperatures and pressures resulting from their proposed correlation. Similar measurements with regard to the R12 + R22 blends are currently in progress for the gaseous phase so as to cover the range of temperatures 298–398 K and of pressures up to about 5 MPa.

### 3. THERMOPHYSICAL PROPERTIES OF CFC ALTERNATIVES

It is needless to emphasize the importance of promoting an extensive research program on the thermophysical properties of essential CFC alternatives, such as R134a and R123, since only scant information generated and distributed by some leading refrigerant manufacturers is available up to the present. The Ministry of International Trade and Industry (MITI), Japan, has recently initiated an R&D Project on Applied Technology with CFC Alternatives. Within this project, it is supposed that three categories of programs including fundamental properties, applied properties, and

safety tests will be included. Thermophysical property studies of CFC alternatives are in progress within the scope of the first category, fundamental properties. An organized task force for the thermophysical properties is being convened by the present author and is composed of several experts from different institutions in Japan. The ongoing research project is an extensive series of measurements of essential thermophysical properties including *PVT* properties, vapor pressures, critical temperature, surface tension, viscosity, and thermal conductivity.

One of the most recent results on the critical parameters of R134a has been reported recently by the group of the present author [35] as the first set of reliable information due to the direct observation. We expect that some additional directly observed results on different essential thermophysical properties both for R134a and R123 will become available in the near-future through the current activities within the task force mentioned above.

#### 4. CONCLUDING REMARKS

The author has attempted to discuss the current status of the thermophysical properties of NARBs, which are recognized to be prospective candidates both for developing the advanced vapor-compression heat pump systems and for finding some additional stratospherically safe refrigerants besides those CFC alternatives earlier proposed. The emphasis, however, has been given to the ongoing research activities in Japan.

Having surveyed the present situation, it is reconfirmed that the absolute quantity of reliable information about thermophysical properties of NARBs is still so much limited that, first of all, we need not only to urge ourselves to speed up our existing research programs but also to encourage our colleagues and experts in related fields of science for their cooperation so as to accumulate our common expertise. Without any systematically observed sets of data which should satisfy the international standards of quality, it becomes less feasible or even almost impossible to establish any rational predictive approach or correlations to meet various demand in industrial applications.

For the last several years, we have been informed of many contributions discussing the prospect of applying NARBs to the heat pump systems. Most of these contributions, however, have dealt with the performance evaluation on the basis of computer simulation associated with the predicted and/or estimated thermophysical property data including VLE data. In this connection, the present author would like to stress the essential importance of examining the predicted results more carefully in view of directly

observed property data so as to deduce reliable conclusions with respect to the system performance.

A recently started program on thermophysical properties of CFC alternatives in Japan has been briefly introduced. In this field of urgent importance, it seems essential to establish an international organization to tackle these time-consuming and elaborate tasks of measuring thermophysical properties. We do need to share our efforts with many experts all over the world in order to retain our globe in a safer and clean condition.

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