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NEARLY AZEOTROPIC MIXTURES TO REPLACE REFRIGERANT 12

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Nearly Azeotropic Mixtures To Replace Refrigerant 12

These mixtures would cause less damage to the ozone layer of the atmosphere.

NASA's Jet Propulsion Laboratory, Pasadena, California

Measurements have indicated that a number of nearly azeotropic fluid mixtures have saturation pressures similar to that of Refrigerant 12 (R12, dichlorodifluoromethane, CCl_2F_2) while being about 2% as damaging as R12 is to the ozone layer in the atmosphere. Moreover, these mixtures are of low toxicity, are nonflammable, and are more compatible with conventional lubricating oils than is Refrigerant 134a (R134a, 1,1,1,2-tetrafluoroethane, CH_2FCF_3; boiling temperature −27.89 °C), which is now the leading replacement for R12. The mixtures may be usable in commercial, automotive, and household refrigerators and air conditioners.

R12, now used in many refrigerators and air conditioners, is known to leak from these machines and ascend into the upper atmosphere, where it damages the ozone layer. One of the proposed replacements, R134a, does not damage the ozone layer because it contains no chlorine. But because of its lack of chlorine, conventional lubricating oils do not dissolve as well in it, and consequently compressors are likely to fail prematurely through nonlubricated wear. Dupont has recently patented an oil-compatible ternary mixture of R22 (chlorodifluoromethane, $CHClF_2$; boiling temperature −40.76 °C), R152a (1,1-difluoroethane, CHF_2CH_3; boiling temperature −25.00 °C), and R124 (2-chloro-1,1,1,2-tetrafluoroethane, $CHClFCF_3$; boiling temperature −12.00 °C). Because the boiling temperatures of these three fluids differ significantly, and because the mixture of them is not azeotropic, leaks could substantially change the composition and, thereby, the pressure characteristics of this fluid.

A thorough search of fluids and hundreds of measurements provided five nearly azeotropic mixtures (see table) of R134a, R152a, R124, and R142b (chlorodifluoroethane, CH_3CClF_2; boiling temperature −9.70 °C) that have low boiling-point spreads, low toxicity, and low ozone-damaging capability, that are nonflammable, and that are more compatible with conventional oils than is R134a. The data from the tests indicate that the pressure of any of the combinations in the table is nearly equal to the pressure of R12, and thus the mixtures may be a good "drop-in substitute" for R12. Because the mixtures are nearly azeotropic, the overall composition should not be significantly altered by leakage.

In addition to R134a, R152a also has no ozone-depletion potential. R124 and R142b both have ozone-depletion potentials that are less than 5 percent of that of R12. Thus all five of the mixtures of the table have ozone-depletion potentials about 2% that of R12. The five mixtures are nonflammable, although R152a and R142b by themselves are flammable. Because R124 and R142b both contain chlorine, they are expected to dissolve oil more effectively than R134a does; the addition of them to R134a is therefore expected to help R134a dissolve conventional lubricating oils.

This work was done by Jack A. Jones of Caltech for **NASA's Jet Propulsion Laboratory.**

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MIXTURES

Mixture Number	Component A	Component B*	Component C*
1	0.5 < R134a < 1.0	R124 < 0.5	
2	0.5 < R134a < 1.0	R142b < 0.5	
3	0.5 < R134a < 1.0	R124 < 0.5	R142b < 0.5
4	0.5 < R134a < 1.0	R152a < 0.5	R124 < 0.5
5	0.5 < R134a < 1.0	R152a < 0.5	R142b < 0.5

*$0.0 < (B + C) < 0.2$
Proportions of component refrigerants are given in mole fractions.

These **Binary and Ternary Nearly Azeotropic Mixtures** of liquids are potential replacements for Refrigerant 12, which is now commonly used. Each of these mixtures has an ozone-depletion potential less than one-hundredth that of Refrigerant 12.

IDENTIFICATION OF COMPONENT REFRIGERANTS

Refrigerant	Formula	Name	Normal Boiling Temperature, °C
R134a	CH_2FCF_3	1,1,1,2-Tetrafluoroethane	−27.89
R152a	CHF_2CH_3	1,1-Difluoroethane	−25.00
R124	$CHClFCF_3$	2-Chloro-1,1,1,2-tetrafluoroethane	−12.00
R142b	CH_3CClF_2	Chlorodifluoroethane	−9.70

LOW-OZONE DAMAGING FLUID MIX SUBSTITUTES FOR REFRIGERANT 12

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aerounatics and Space Administration.

ABSTRACT

Test measurements made at JPL have indicated a number of near-azeotropic fluid mixtures have saturation pressures similar to Refrigerant 12, but the mixtures are at least 100 times less damaging to the earth's ozone layer. Furthermore, the mixtures are of low toxicity, are non-flammable, and are likely to have an improved coefficient of performance and better compatibility with oil than Refrigerant 134a, the present leading replacement for Refrigerant 12. Although the newly discovered JPL blends are likely to cost more than the recently patented Dupont ternary blend, they are at least four times less ozone-damaging than the Dupont blend, and they are at least twice as azeotropic.

INTRODUCTION

Earlier in the earth's history, before the stratospheric ozone layer had formed, animals and plants were mostly confined to a protective underwater environment. As plants generated oxygen, which slowly diffused up to the stratosphere, a protective ozone layer was built which absorbed harmful ultraviolet (UV) radiation. As stated by Shell (Reference 1), "Living things were then able to climb out of the primordial slime and onto land." We have ever since been blessed with nature's stratospheric "sunscreen". In 1974, however, F. Sherwood Rowland, a chemist at the University of California, Irvine and Mario Molina, then a postdoctoral fellow and now a senior research scientist at JPL, became the first two people to document the potential catastrophic destruction of the earth's ozone layer by man's chlorofluorocarbon (CFC) release into the atmosphere (Ref. 2). The chlorine in CFCs acts as a catalyst in the breakdown of ozone. A single atom of chlorine can help turn tens of thousands of ozone molecules into an impotent pile of oxygen molecules.

Rowland and Molina's theories have more recently been confirmed, with the recent discovery of ozone "holes" both over the Arctic and the Antarctic and a reduction of as high as 5% (over the last 17 years) of the ozone layer over latitudes corresponding to the United States (Ref. 3). There is, in fact, strong evidence that human skin cancer rates have already started to soar (Ref. 1), and that the ocean's phytoplankton, which is the very basis of the earth's food chain, has been reduced by 25%. The phytoplankton, which live very near to the ocean's surface, are not afforded the same UV protection that lower living fish and plants have. There is also evidence that the earth's climate is warming up due to the "greenhouse effect" resulting from man's dumping of CFC's and other infrared-trapping gases into the atmosphere.

PROTECTIVE LEGISLATION

Starting from the time CFC's were first discovered by Thomas Midgely of General Motors in 1928 until 50 years later, CFC's had routinely been used as aerosol propellants, industrial cleaners, foam insulation, and as refrigerants. In 1978, however, the U.S. Environmental Protection Agency (EPA) announced that it was phasing out the use of CFC's for most nonessential aerosol propellants (Ref. 4). Then, on September 16, 1987, a landmark international agreement to protect the ozone layer was completed in Montreal, Canada (Ref. 5). The agreement, known as the "Montreal Protocol" was negotiated under the sponsorship of the United Nations Environment Programme (UNEP). It sets up a worldwide process to control substances that could deplete the ozone layer, and calls for a reduction in consumption and production in 1993 to 80% of the level of 1986 CFC's, and a further reduction to 50% of the 1986 level by 1998.

Numerous other legislative proposals have been submitted, including a total ban of common air conditioners for automobiles (Ref. 6). It seems more likely, however, that alternative refrigeration systems can reduce CFC consumption, as alternatives to CFC's are now in the process of doing for the aerosol, industrial cleaner, and foam insulation industries.

POSSIBLE SUBSTITUTES FOR R12

Numerous researchers have proposed alternatives that eliminate the use of R12, which is the most commonly used refrigerant for automobile air conditioners and other systems. Alternate refrigeration cycles, such as absorption cycles, Stirling cycles, evaporative cooling, etc. have been proposed, but none seems to have the overall efficiency, versatility, economy and long-life inherent in the traditional J-T cooling refrigeration cycle. Thus, an alternative refrigerant seems to be the answer.

The Montreal Protocol is applied specifically to R11, R12, R13, R113, R114, and R115, all of which have an extremely long life expectancy in the atmosphere, and which can thus slowly diffuse to the stratosphere and wreak havoc with the ozone. Other refrigerants, which have no chlorine or which are more readily decomposed in the atmosphere, pose little or no danger to the earth's ozone layer.

No single refrigerant is known that can adequately replace R12. The closest single substitute to R12, in terms of being non-toxic, non-flammable, and non-ozone-damaging is R134a. This refrigerant, however, contains no chlorine at all, and since chlorine makes CFC's soluble in oils, R134a is not soluble in the present lubricating oils used to lubricate the compressors. Furthermore, R134a is not quite as energy-efficient as R12. Although it is rather expensive (expected bulk cost will be 3 to 5 times that of R12), it is still the present leading contender as a replacement for R12, assuming adequate soluble lubricating oils are discovered.

Numerous fluid mixtures have been proposed that overcome R134a's disadvantages. These mixtures generally fall into the category of azeotropic or non-azeotropic. For an azeotropic mixture, the mixture's properties do not change with evaporative leakage. Since most air conditioning systems do, in fact, tend to leak, with time, it seems that an azeotropic or near-azeotropic mixture would be desired. The number of fluids suggested for mixing the replicate R12 properties is limited for a variety of reasons (to be discussed in the next section). Seven researcher groups have proposed using the various fluids listed in Table 1 as potential fluid mixture replacements for R12 (Ref. 8-14). **With the exception of the Dupont mixture, which was recently patented, there has been absolutely <u>no</u> publication of any azeotropic or near-azeotropic mixture data for potential R12 substitutes.** The Dupont blend, which mixes R22, R152a, and R124, has an ozone depletion potential of about twenty times less than R12, it is non-flammable, and is expected to be non-toxic (toxicity studies in progress for R124). Although the blend is non-azeotropic, its vapor pressure only changes by about 9.4% with a 50% leakage, and thus it may be acceptable for commercial use. Its oil-compatibility is better than R134a and the blend is expected to be considerably cheaper.

The goal of this project, then, has been to find an azeotropic or near azeotropic blend of fluids that surpasses both R134a and the Dupont mixture.

POTENTIAL FLUID MIX CANDIDATE SELECTIONS

Table 2 contains a listing of all potential fluids that have normal boiling point (NBP's) from -82°C to -5°C. Next to each fluid is listed acceptance or rejection comments. In summary, of all the fluids considered, only six appear to be acceptable in terms of cost, toxicity, ozone-damage-potential, other environmental damage potential and relative flammability. These six are R23, R22, R134a, R152a, R124, and R142b. A seventh fluid, R134, was also selected for testing, even though its toxicity data is unknown since it was felt that its properties were likely to be very similar to R134a, which was not immediately available at the commencement of testing.

Although the total number of binary, ternary, and quaternary combinations of these seven fluids is over 1000, by selectively choosing binary combinations that were considered "most-likely-to-succeed" in forming acceptable azeotropes, the binary field was reduced from 42 combinations to 17 combinations. Based on these results, the "most-likely-to-succeed" ternary combinations were then reduced from 210 to 5, and the quaternaries were subsequently reduced from 840 to only 1. Thus the total number of actual combinations tested was reduced to only 23.

It should be mentioned that we attempted to discover only the more common positive or negative azeotropes, and thus the far less common saddle azeotrope (similar to the Dupont blend near-azeotrope) would not be detected in the aforementioned methodology.

TEST PROCEDURE

A relatively simple test to determine the existence of a binary azeotrope is to measure the pressure of a binary mixture at various concentrations of one component in the other at a fixed temperature (Ref. 15). A maximum in the vapor-pressure curve of the binary mixture is indicative of a minimum-boiling azeotrope while a minimum in the vapor-pressure curve of the binary mixture is indicative of a maximum constant-boiling mixture. In Figures 1 and 2 are plotted typical curves of the former and latter type, respectively. The straight lines in each figure are the partial pressures of each component of the solution calculated from Raoult's law for ideal gases. The sum of the ordinates of these two lines, shown dotted and designated at A + B, is the vapor pressure of the mixture predicted from Raoult's law. The actual vapor-pressure curve of the mixture in Figure 1 shows a maximum at Z, while in Figure 2, the vapor-pressure curve of the binary mixture shows a minimum at Z.

Deviations of mixture pressure from the ideal dashed line in Figures 1 and 2 are caused by intermolecular interactions between the two fluids. If the real mixture pressure was in fact, the dashed line, then the more volatile component A, would preferentially boil, and a vapor leakage would eventually result in only component B remaining in the system.

Near-azeotropic mixtures are mixtures that almost have a maximum or minimum point, i.e. the slopes of the pressure curves are very small. Ternary azeotropes (mixtures of three fluids) have maximum or minimum pressures at some combination of all three fluids.

The test fixture shown in Figure 3 (sketch) and Figure 4 (Photo) was fabricated and numerous potential fluids were purchased. The fluid mole fractions, as determined by pressure additions to the transfer volume, were mixed and allowed to condense in the 0°C (+0.1/-0.0°C) ice bath. The pressure was then measured for a number of separate mole fraction ratios for each mixture.

As a test of this procedure, a known azeotrope, R500, was tested. R500 is an azeotropic mixture consisting of 74% R12 plus 26% R152a. Our data (Figure 5) does, in fact, indicate that an azeotrope occurs, although the indications are that it occurs at about 30+% R152a. Azeotrope mixture combinations are known to vary somewhat with temperature, and thus our measurements at 0°C seem to be reasonable compared to the reported valve which was likely taken at room-temperature.

RESULTS AND CONCLUSIONS

The results of seventeen binary mixture combinations are shown in Figures 6-22 with an additional 5 ternary mixture combinations in Figures 23-27 and a final quaternary mixture combination in Figure 28. Other than the known azeotrope of R12 and R152a previously tested (Figure 5), none of the other fluids exhibit an actual minimum or maximum pressure occurrence. Numerous fluid combinations, however, have nearly flat pressure characteristics in the pressure range of R12, i.e. about 44.7 psia, and thus can be considered to be "near-azeotropic".

The six candidate mixtures that have been selected from this data as potential "drop-in" substitutes for R12 are listed in Table 3 (possible patent pending-Ref.15). Basically, all the combinations include at least 80% R134a with the remaining **20%** to be constituted from one or more of refrigerants R124, R142b, and R152a. All of these combinations are expected to be non-toxic, non-flammable, and near-azeotropic. Toxicity studies are completed for R152a and R142b and are scheduled for completion for R134a around 1992 and for R124 shortly thereafter. Furthermore, all combinations should be more oil-compatible than R134a, due to the existence of chlorine in R124 and R142b.

It should be noted that at room temperature or above, the vapor pressure of R134a is actually slightly **higher** than R12, and thus at higher temperatures, the six candidate mixtures should actually be expected to more closely approximate R12 than does R134a by itself. In addition, it has been noted that the coefficient of performance (COP) is lower for R134a than for R12, but that the COP of R152a is actually **better** than that for R12 (Ref. 16). Thus, combinations of R152a and R134a will more likely approximate the COP of R12 than does R134a by itself. A possible optimum ternary blend for near term use might consist of R134a (toxicity tests to be completed in 1992) + R142b (for oil compatibility) + R152a (for improved COP).

All the listed JPL/CalTech mixtures are expected to be at least <u>100 times</u> less damaging to ozone than R12, as compared to the Dupont mixture (Ref. 8), which is only about <u>25 times</u> less damaging than R12. Furthermore, the JPL mixtures tend to be at least twice as azeotropic as the Dupont mixture. Dupont reports a 9.4% pressure drop with a 50% leakage, whereas a measurement of one of the new mixtures (typical of the other mixtures) shows about a 4% pressure drop, or less, depending on the relatively constituency amount of R134a (Fig. 29).

It should be noted that the JPL/CalTech blends are likely to be more expensive than the Dupont blend, since the cost of the primary JPL constituent, R134a, is expected to be 3-5 times that of R22, which is the primary Dupont constituent. The JPL/CalTech blends, however, have advantages of being over twice as azeotropic and having over four times lower ozone-depletion-potential than the Dupont blend. **Further expedient testing and development of these new blends are therefore very strongly urged.**

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*PLEASE OBTAIN REFERENCES FROM THE SOURCES LISTED.

Table 1. R12 Fluid Mix Substitute Literature Search

Refrig	Chem Formula	Name	($^{\circ}$C) NBP	Ref 8 Dupont	Ref 9 Midwest	Ref 10 McLinden	Ref 11 Creswick	Ref 12 Vineyard	Ref 13 Kruse	Ref 14 Weisfeld
R23	CHF_3	Trifluoromethane	-82.06						X	
R32	CH_2F_2	Methylene Fluoride	-51.61					X		
R125	CHF_2CF_3	Pentafluoroethane	-48.50		X		X	X		
R143a	CH_3CF_3	Trifluoroethane	-47.61				X	X		
R22	$CHClF_2$	Chlorodifluoromethane	-40.76	X	X	X		X	X	X
R218	$CF_3CF_2CF_3$	Octafluoropentane	-39.00		X			X		
R12	CCl_2F_2	Dichlorodifluromethane	-29.79							
R1113	$CClF=CF_2$	Chlorotrifluoroethylene	-27.89		X					
R134a	CH_2FCF_3	1,1,1,2-Tetrafluoroethane	-26.50		X	X				X
R152a	CHF_2CH_3	1,1-Difluoroethane	-25.00	X		X	X		X	X
R134	CHF_2CHF_2	1,1,1,2-Tetrafluoroethane	-19.72			X				
R124	$CHClFCF_3$	2-Chloro-1,1,1,2-Tetrafluoroethane	-12.00	X	X		X	X		X
R124a	CHF_2CClF_2	1-Chloro-1,1,1,2-Tetrafluoroethane	-10.22		X			X		
R142b	CH_3CClF_2	Chlorodifluoroethane	-9.7		X		X	X	X	
R318	C_4F_8	Octafluorocyclobutane	-5.83		X			X		
R31.10	$CF_3CF_2CF_2CF_3$	Perfluorobutane	-5.00		X					

Table 2. Potential R12 Replacement Fluid Mix Selections

Refrig	Chem Formula	Name	(°C) NBP	Accept/ Reject	Comments
23	CHF_3	Trifluoromethane	-82.06	A	Very low NBP (unlikely good azeo)
13	$CClF_3$	Chlorotrifluoromethane	-81.44	R	Ozone damage
116	CF_3CF_3	Hexfluoroethane	-78.50	R	Greenhouse effect
744	CO_2	Carbon Dioxide	-78.44	R	Possibly reactive
41	CH_3F	Methyl Fluoride	-78.39	R	Very flammable
1114	$CF_2=CF_2$	Tetrafluoroethane	-76.28	R	Reactive
1141	$CH_2=CHF$	Vinyl Fluoride	-72.22	R	Reactive
-	SF_6	Sulfur Hexafluoride	-63.78	R	Toxic
13B1	$CBrF_3$	Bromotrifluoromethane	-57.75	R	Toxic
504	R32/R115	(Azeotrope)	-57.22	R	Ozone damage
32	CH_2F_2	Methylene Fluoride	-51.61	R	Flammable (unlikely good azeo)
1123	$CF_2=CHF$	Trifluoroethane	-51.00	R	Reactive
125	CHF_2CF_3	Pentafluoroethane	-48.50	R	Too expensive
1270	$CH_2=CHCH_3$	Propylene	-47.70	R	Flammable. Toxicity unknown.
143a	CH_3CF_3	Trifluoroethane	-47.61	R	Possibly toxic
502	R22/R115	(Azeotrope)	-45.44	R	Ozone damage
290	$CH_3CH_2CH_3$	Propane	-42.07	R	Very flammable
22	$CHClF_2$	Chlorodifluoromethane	-40.76	A	Low ozone damage
115	$CClF_2CF_3$	Chloropentafluoroethane	-39.11	R	Ozone damage
218	$CF_3CF_2CF_3$	Octafluoropropane	-39.00	R	Greenhouse effect
161	CH_3CH_2F	Fluoroethane	-37.22	R	Very flammable
500	R12/R152a	(Azeotrope)	-33.50	R	Ozone damage
C270	$CH_2CH_2CH_2$	Cyclopropane	-33.50	R	Very flammable
717	NH_3	Ammonia	-33.33	R	Toxic
C216	$CF_2CF_2CF_2$	Perfluorocyclopropene	-31.50	R	Greenhouse effect
12	CCl_2F_2	Dichlorodifluoromethane	-29.79	R	Ozone damage
505	R12/R31	(Azeotrope)	-29.61	R	Ozone damage
1216	$CF_2=CFCF_3$	Perfluoropropane	-29.00	R	Reactive
1132	$CHF=CHF$	1,2-Difluoroethane	-28.00	R	Reactive
1113	$CClF=CF_2$	Chlorotrifluoroethylene	-27.89	R	Reactive
134a	CH_2FCF_3	1,1,1,2-Tetrafluoroethane	-26.50	A	Toxicity tests in progress
152a	CHF_2CH_3	1,1-Difluoroethane	-25.00	A	Slightly flammable

Table 2. Potential R12 Replacement Fluid Mix Selections (Continued)

Refrig	Chem Formula	Name	(°C) NBP	Accept/ Reject	Comments
40	CH_3Cl	Methyl Chloride	-24.22	R	Toxic
1131a	$CClF=CH_2$	1-Chloro-1-fluoroethane	-24.00	R	Reactive
1261ya	$CH_3CF=CH_2$	2-Fluoropropene	-24.00	R	Reactive
115B1	$CBrF_2CF_3$	Bromopentafluoroethane	-22.00	R	Toxic
1225zc	$CF_3CH=CF_2$	1,1,1,3,3-Pentafluoropane	-21.00	R	Reactive
134	CHF_2CHF_2	1,1,2,2-Tetrafluoroethane	-19.72	A	Toxicity unknown (sim to R134a?)
1122	$CHCl=CF_2$	1-Chloro-2,2-Difluoroethane	-18.48	R	Reactive
227ea	CF_3CHFCF_3	1,1,1,2,3,3,3-Heptafluoropropane	-18.00	R	Toxicity unknown
1243zf	$CF_3CH=CH_2$	1,1,1-Trifluoropropane	-18.00	R	Reactive
245cb	$CF_3CF_2CH_3$	1,1,1,2,2-Pentafluoropropane	-17.72	R	Toxicity unknown
227ca	$CF_3CF_2CHF_2$	1,1,1,2,2,3,3-Heptafluoropropane	-17.00	R	Toxicity unknown
22B1	$CHBrF_2$	Bromodifluoromethane	-15.00	R	Toxic
1140	$CHCl=CH_2$	Chloroethane	-13.89	R	Reactive
506	R31/R114	(Azeotrope)	-12.44	R	Ozone damage
124	$CHClFCF_3$	2-Chloro-1,1,1,2-Tetrafluoroethane	-12.00	A	Low ozone damage
600a	C_4H_{10}	Isobutane	-11.73	R	Very flammable
124a	CHF_2CClF_2	1-Chloro-1,1,2,2-Tetrafluoroethane	-10.22	R	Toxicity unknown
764	SO_2	Sulfur Dioxide	-10.00	R	Toxic
142b	CH_3CClF_2	Chlorodifluoroethane	-9.78	A	Low ozone damage
281ea	CH_3CHFCH_3	2-Fluoropropane	-9.39	R	Very flammable
31	CH_2ClF	Chlorofluoromethane	-9.11	R	Toxic
630	CH_3NH_2	Methylamine	-6.72	R	Very flammable
C318	C_4F_8	Octafluorocyclobutane	-5.83	R	Greenhouse effect
31.10	$CF_3CF_2CF_2CF_3$	Perfluorobutane	-5.00	R	Greenhouse effect
1122a	$CClF=CHF$	1-Chloro-1,2-Difluoroethane	-5.00	R	Reactive

Table 3. JPL Near-Azeotropic Mixture Replacements for R12

Mixture	Component A	Component B*	Component C*	Component D*
1	0.8<R134a<1.0	R124<0.2		
2		R142b<0.2		
3		R124<0.2	R142b<0.2	
4		R152a<0.2	R124<0.2	
5		R152a<0.2	R142b<0.2	
6		R124<0.2	R142b<0.2	R152a<0.2

*0.0<(B+C+D)<0.2

All fractions are given as molefractions

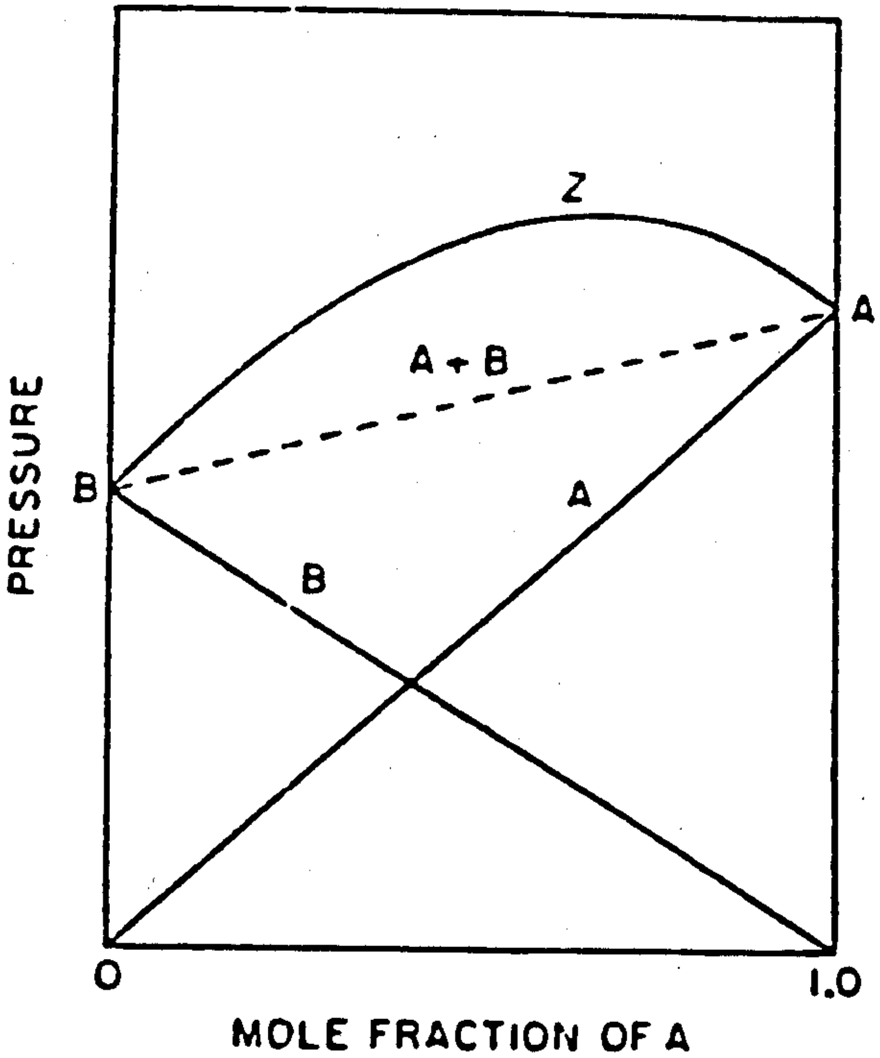


FIGURE 1 MINIMUM-BOILING AZEOTROPIC CHARACTERISTICS

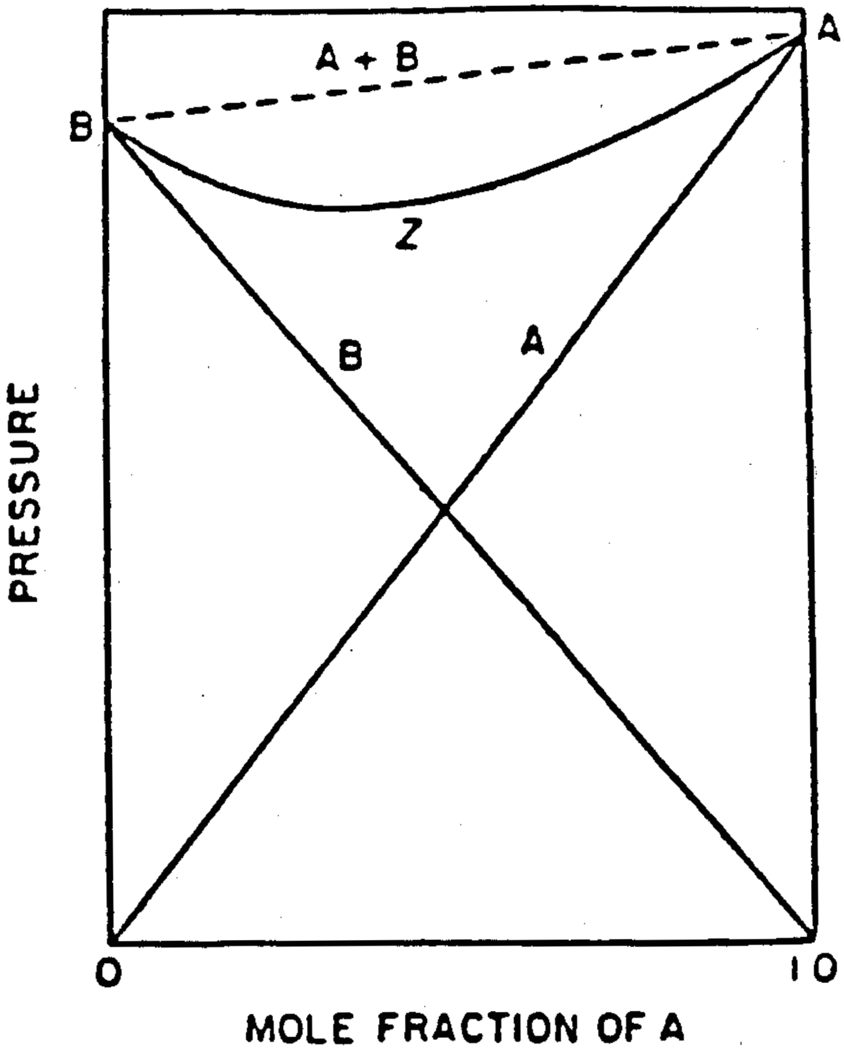


FIGURE 2 MAXIMUM-BOILING AZEOTROPIC CHARACTERISTICS

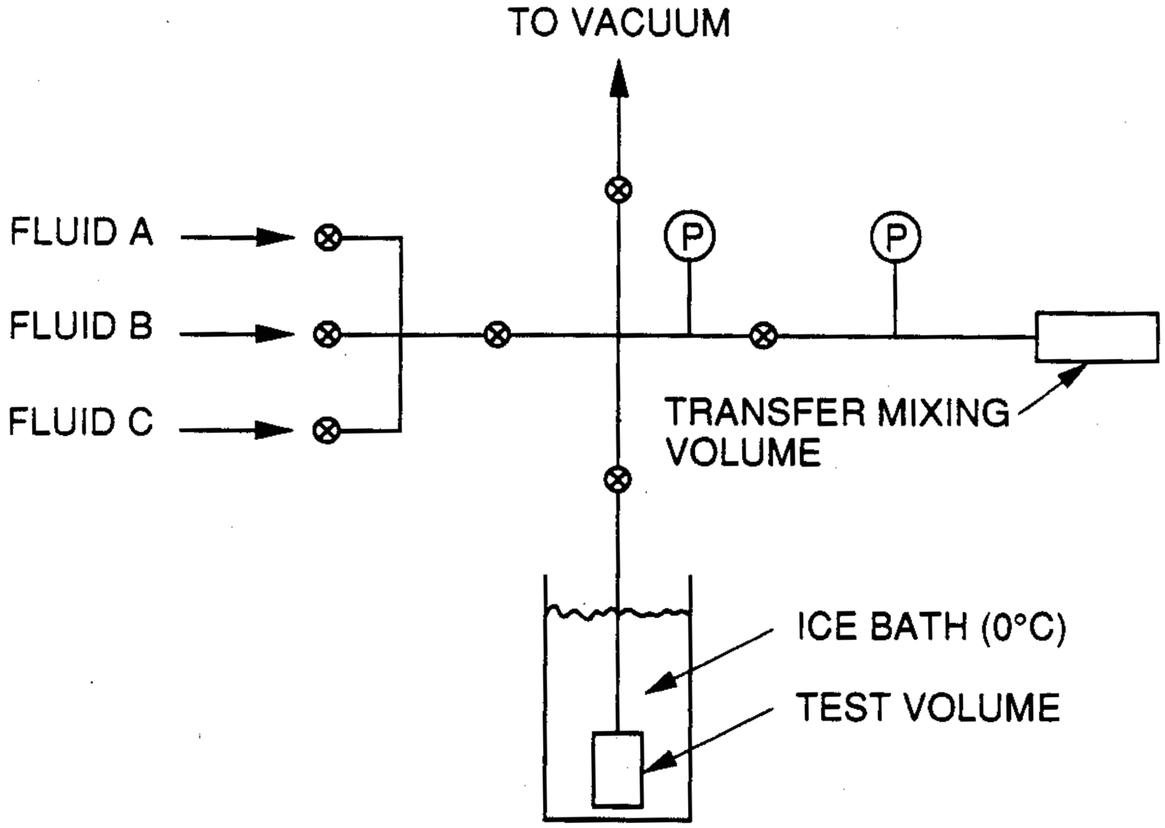


FIGURE 3 AZEOTROPIC GAS MIX TEST APPARATUS SKETCH

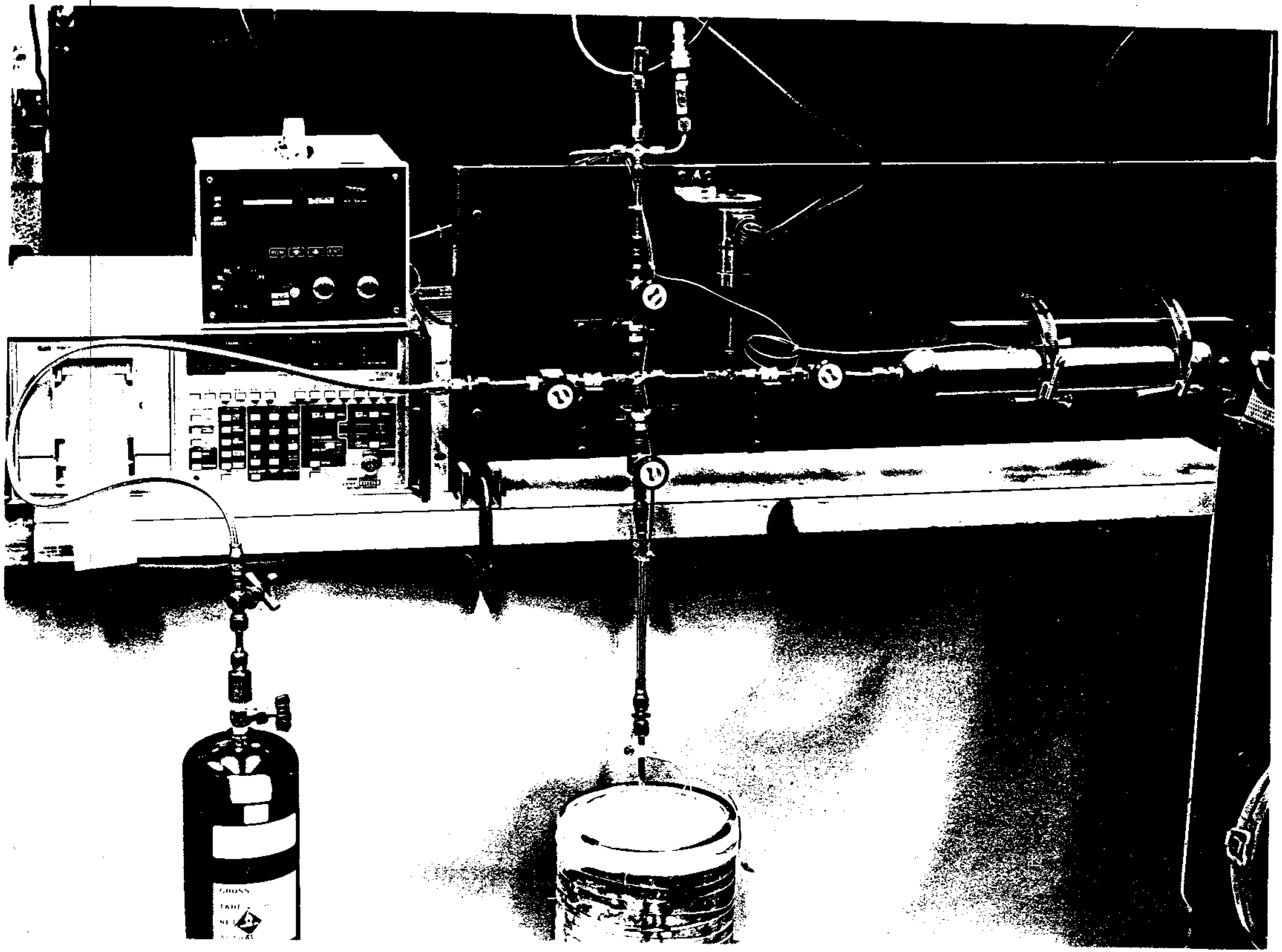


FIGURE 4 AZEOTROPIC GAS MIX TEST APPARATUS PHOTO

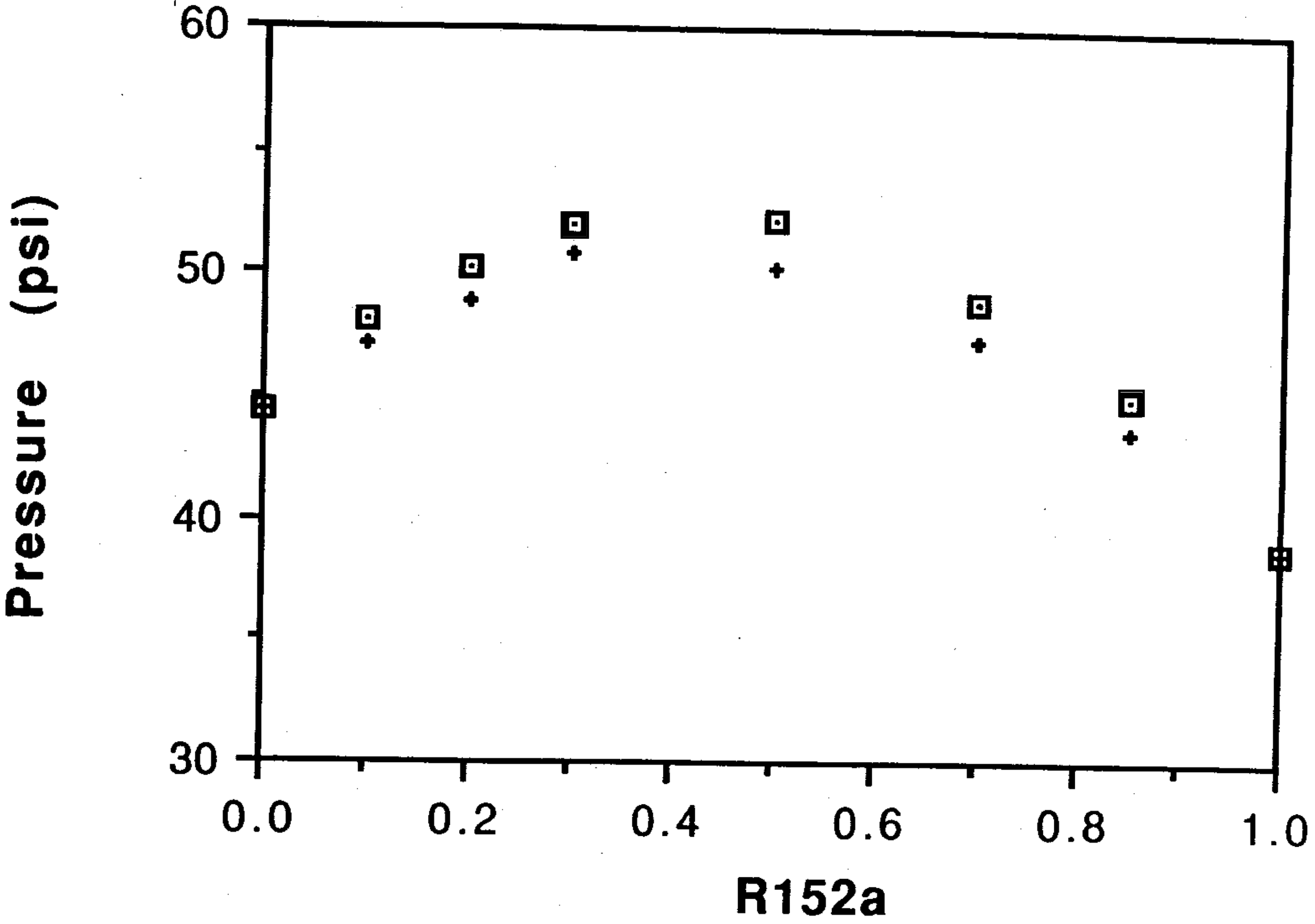


FIGURE 5 TEST DATA CONFIRMING KNOWN AZEOTROPE (R500)

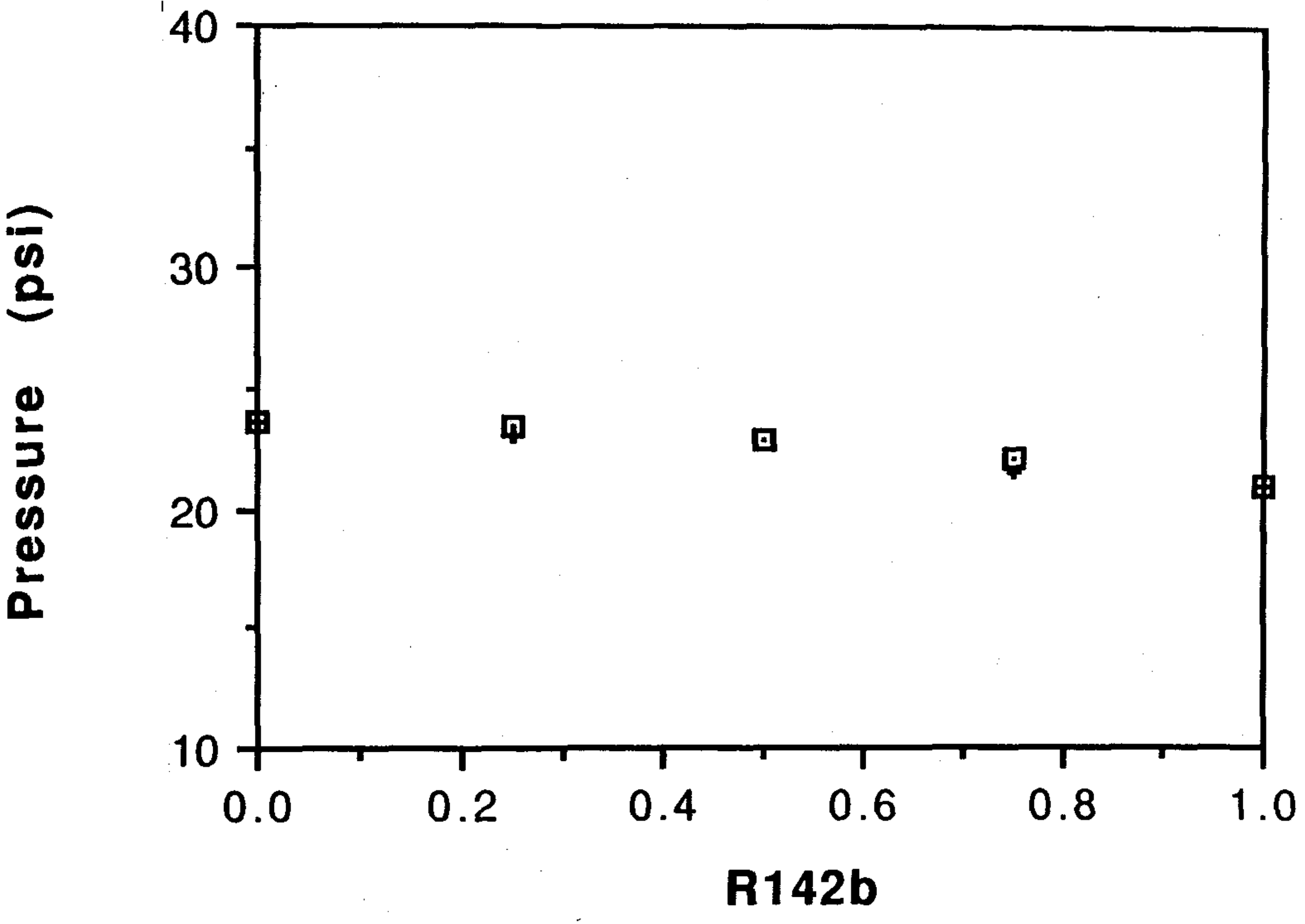


FIGURE 6 BINARY MIXTURE OF R124 + R142B

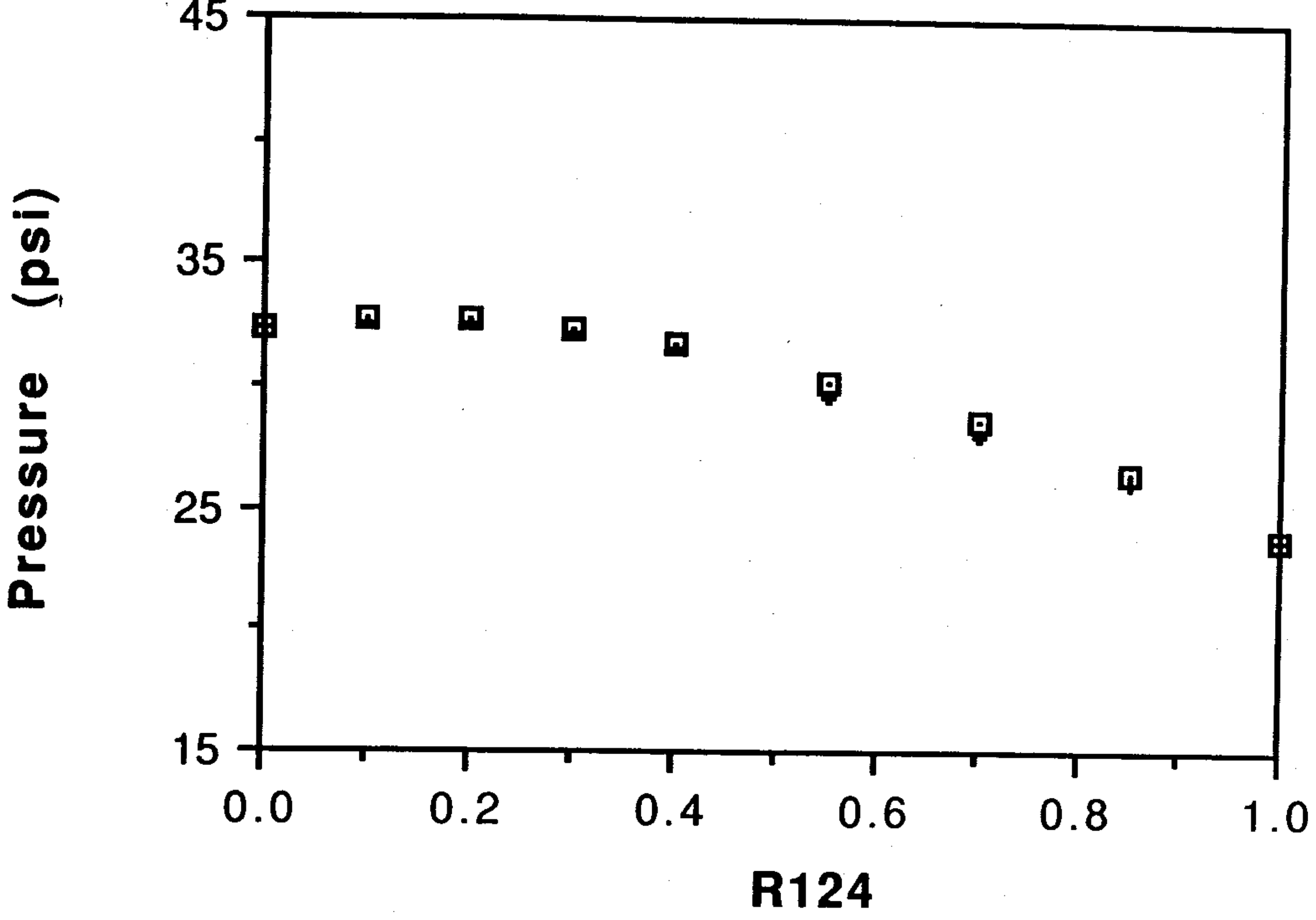


FIGURE 7 BINARY MIXTURE OF R134 + R124

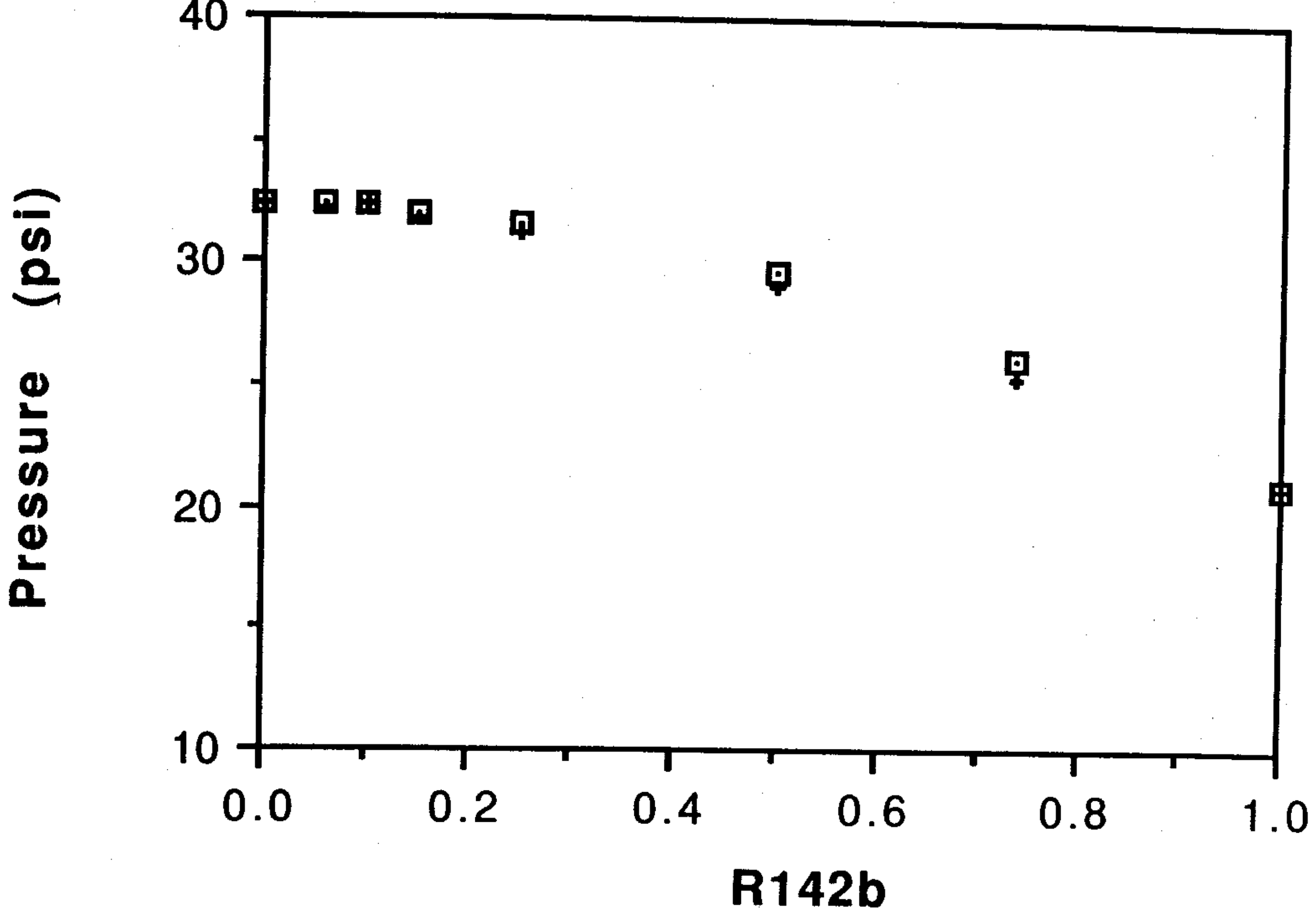


FIGURE 8 BINARY MIXTURE OF R134 + R142B

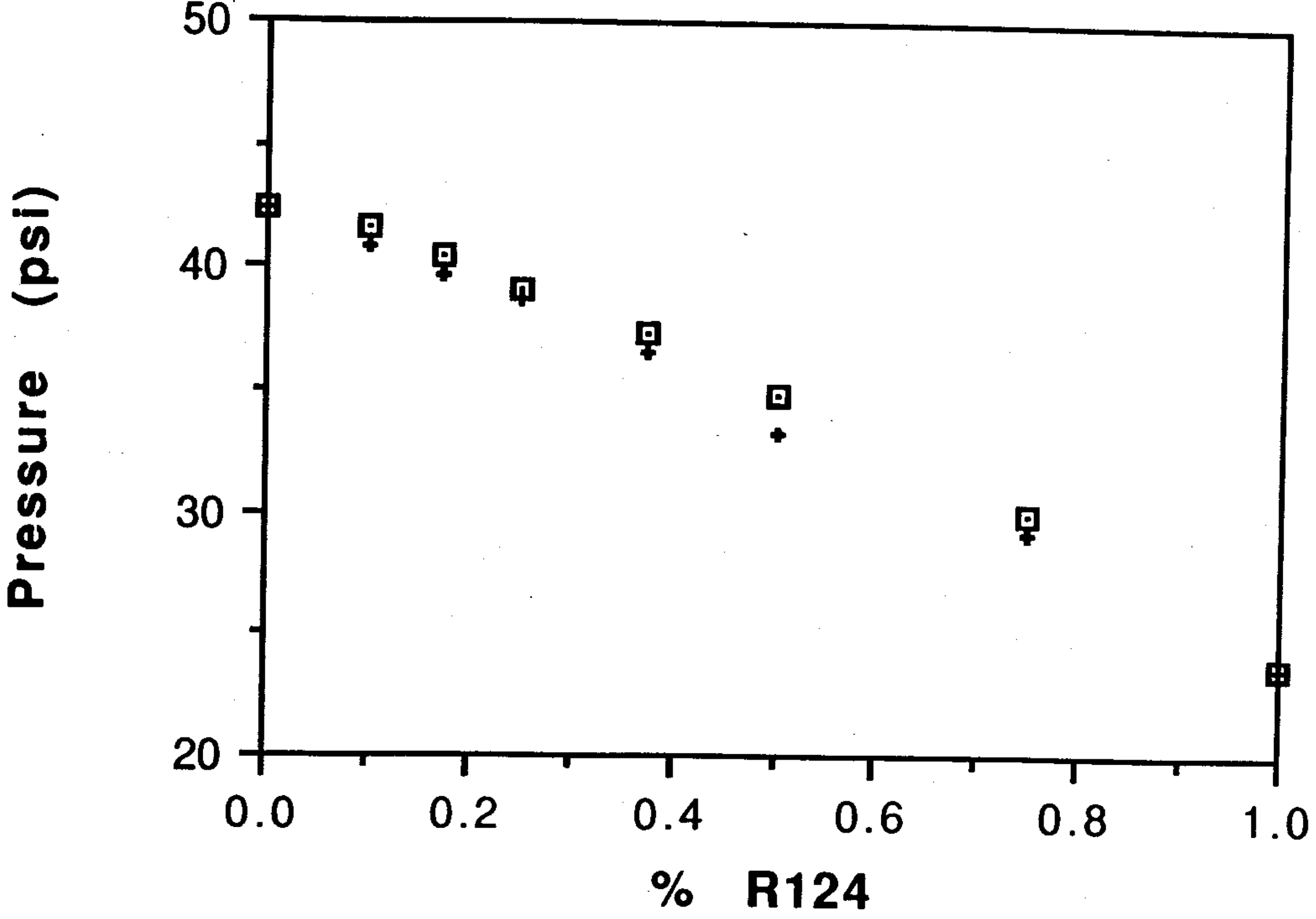


FIGURE 9 BINARY MIXTURE OF R134A + R124

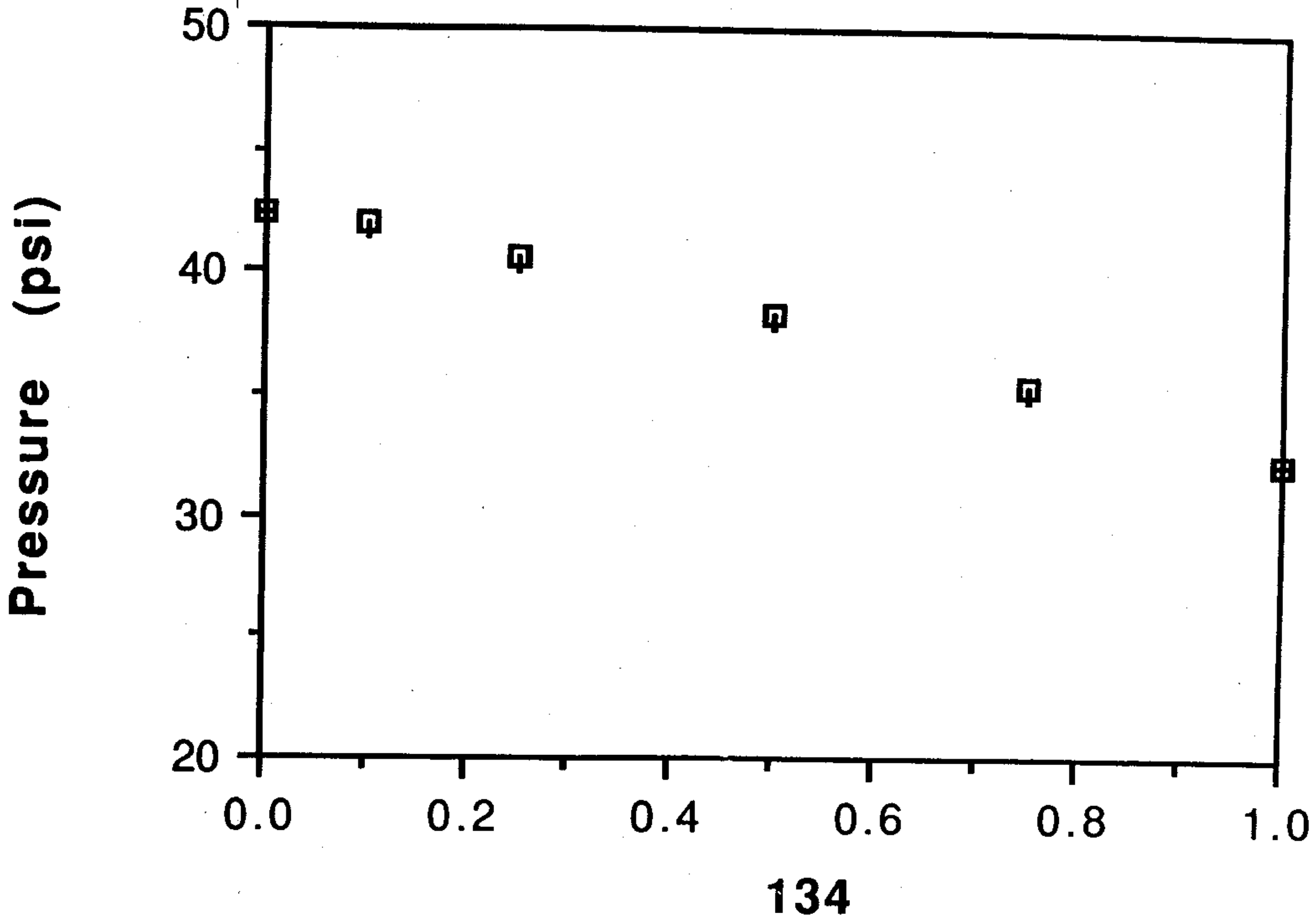


FIGURE 10 **BINARY MIXTURE OF R134A + R134**

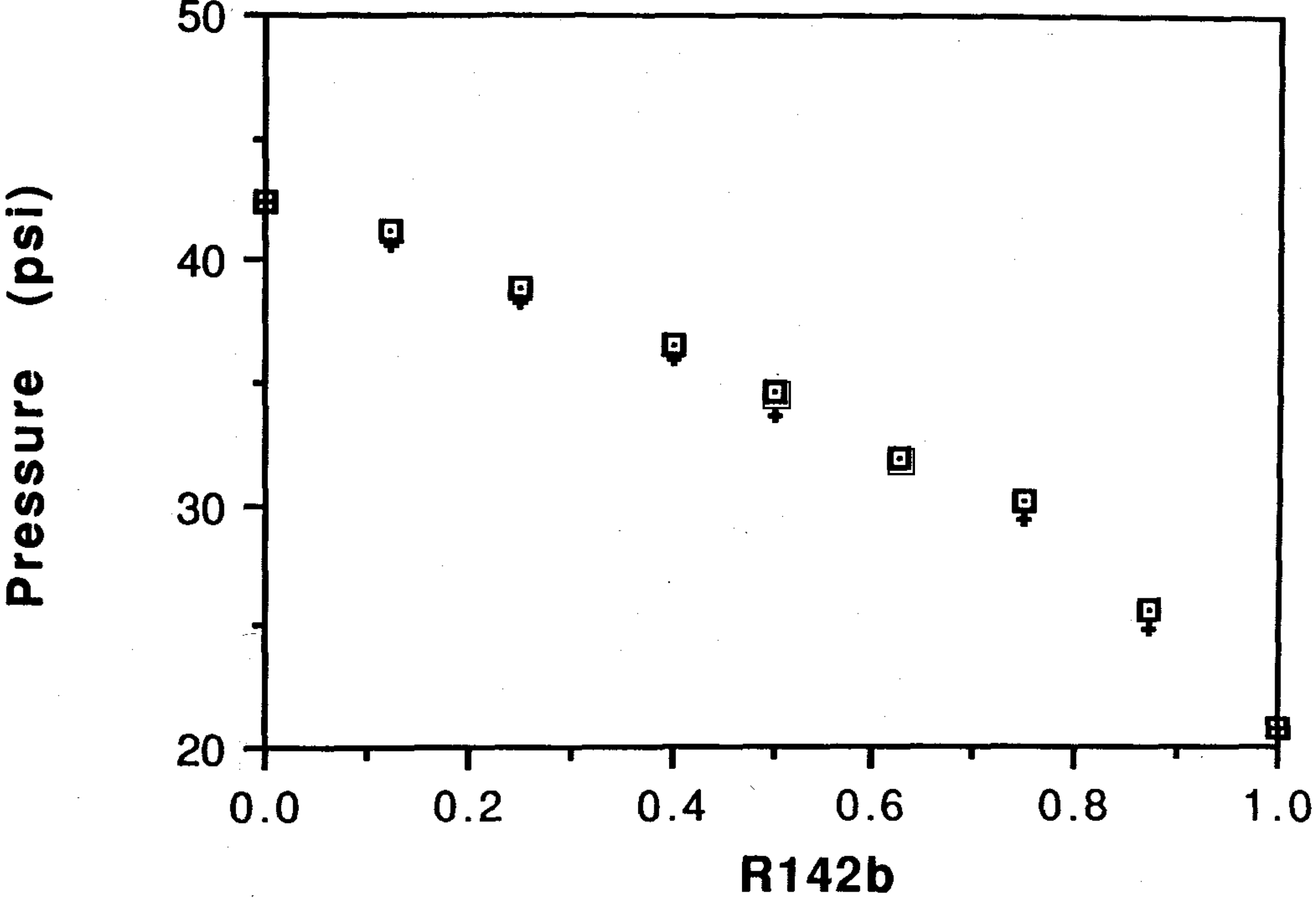


FIGURE 11 BINARY MIXTURE OF R134A + R142B

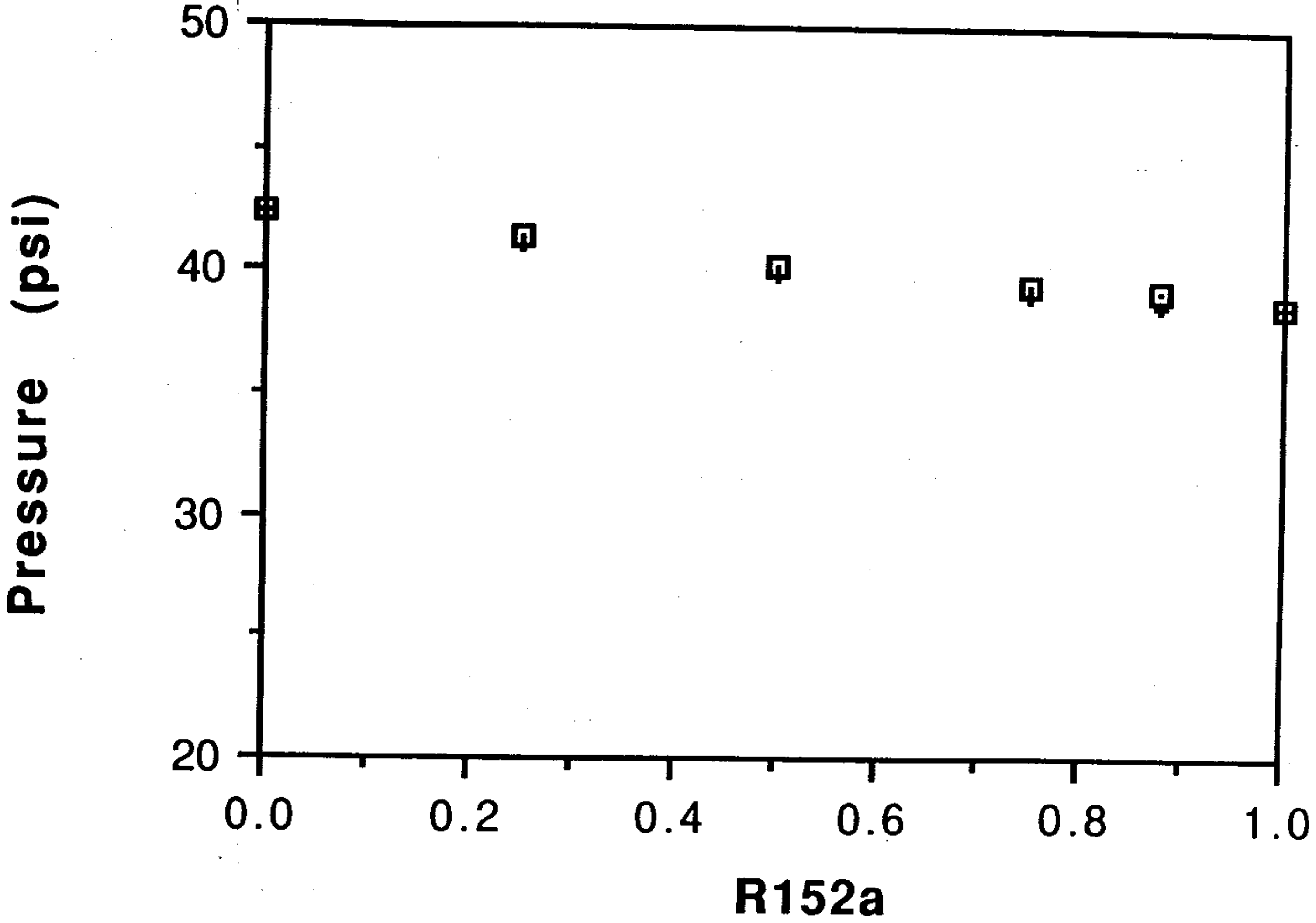


FIGURE 12 BINARY MIXTURE OF R134A + R152A

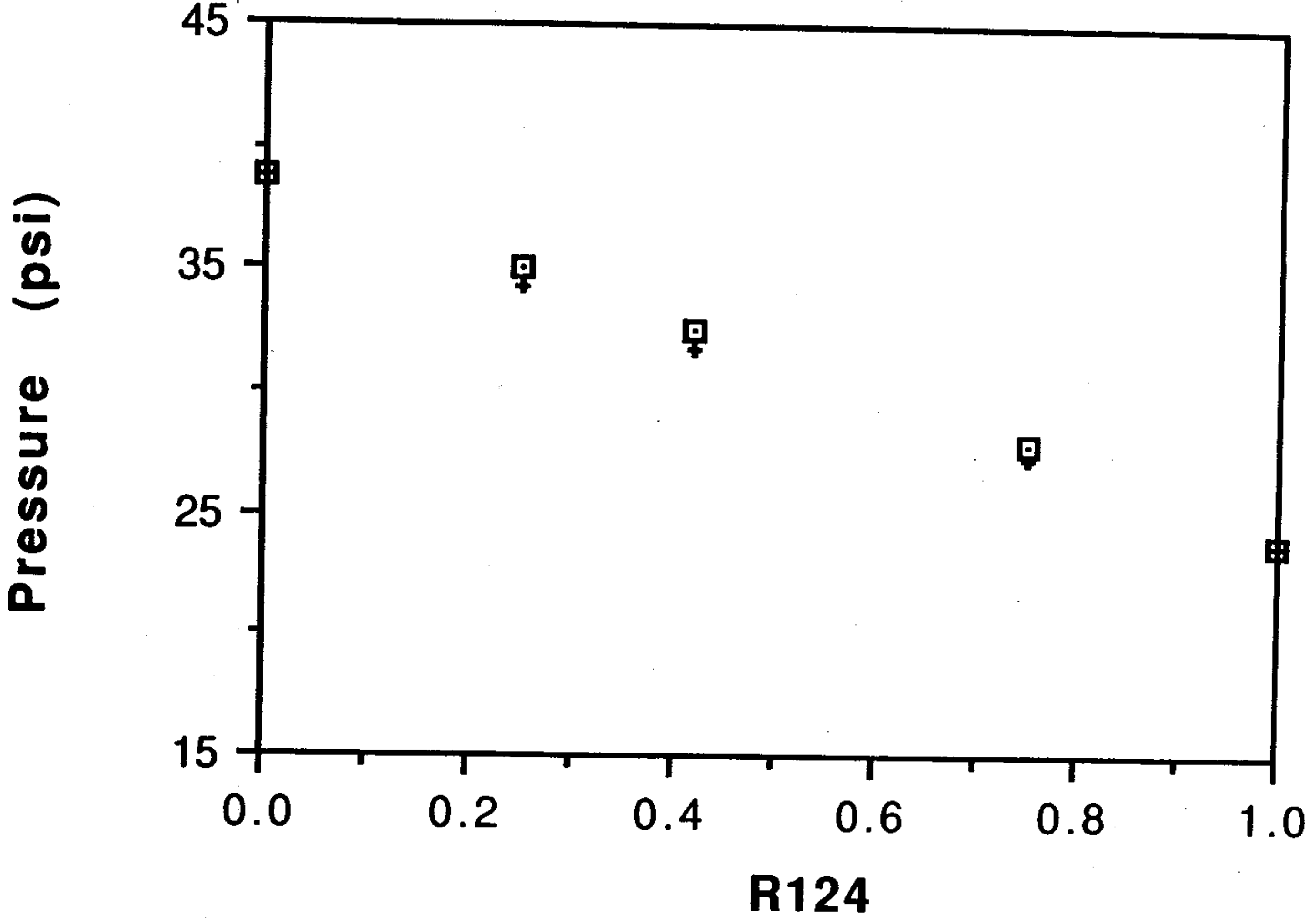


FIGURE 13 BINARY MIXTURE OF R152A + R124

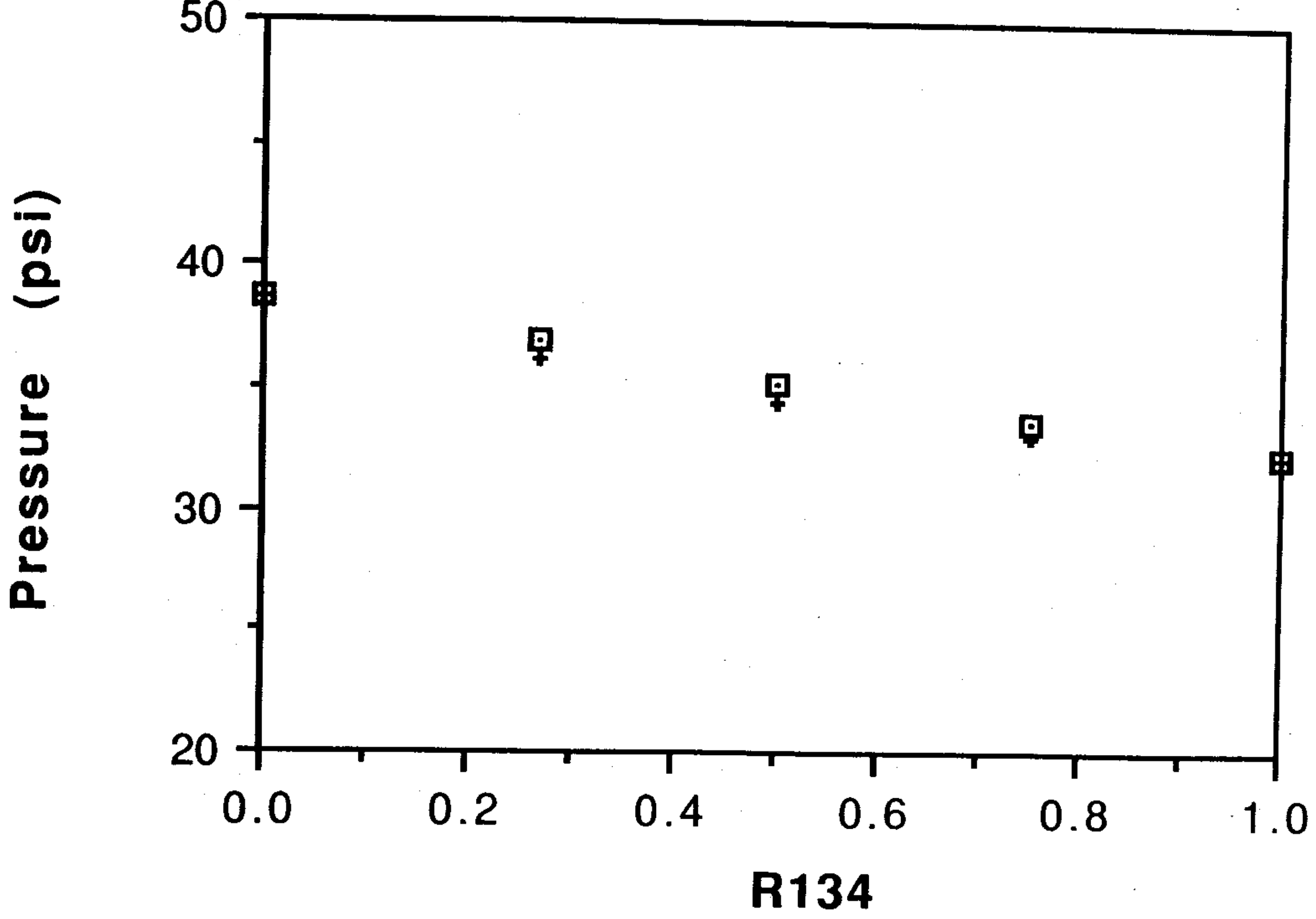


FIGURE 14 BINARY MIXTURE OF R152A + R134

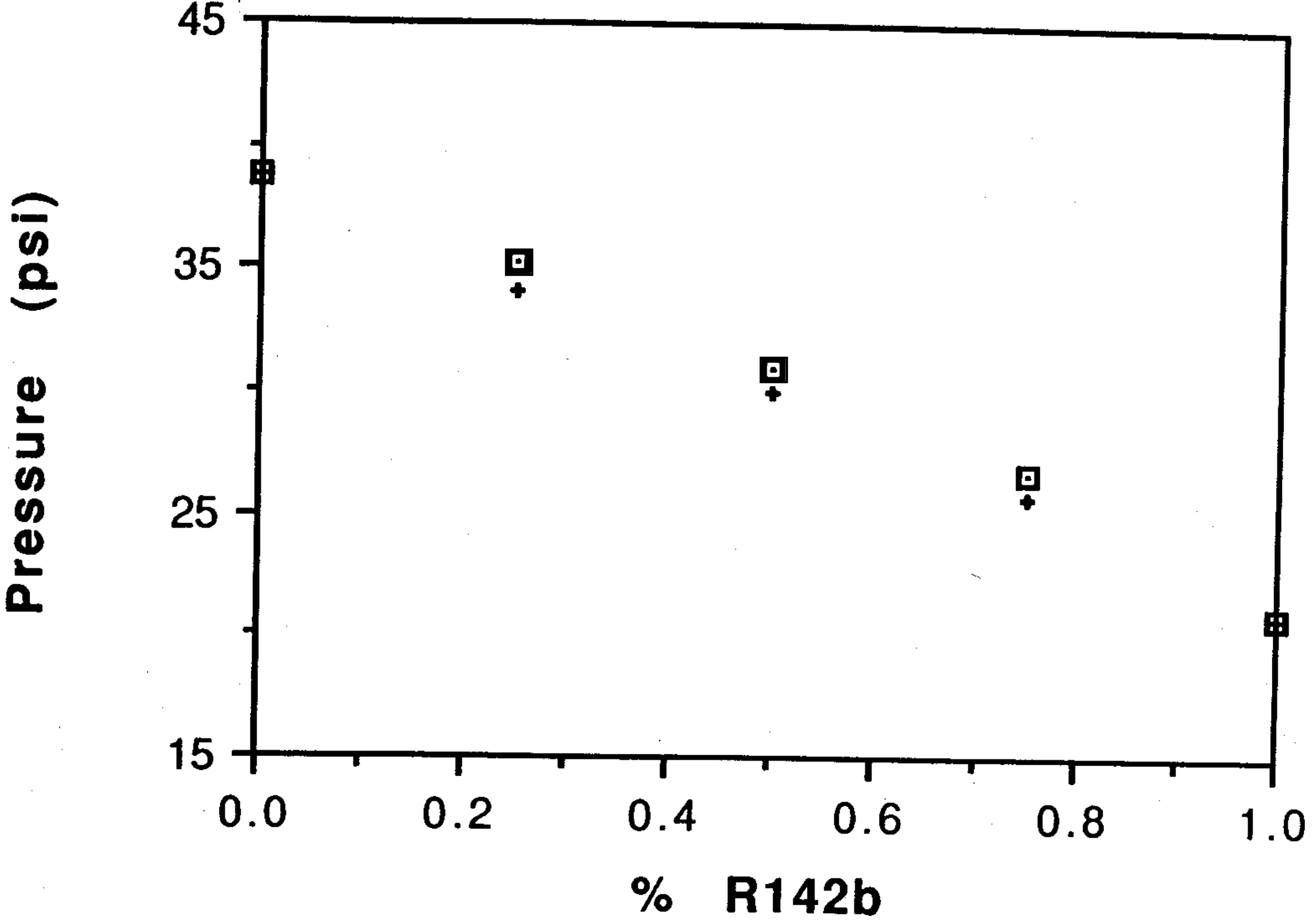


FIGURE 15 BINARY MIXTURE OF R152A + R142B

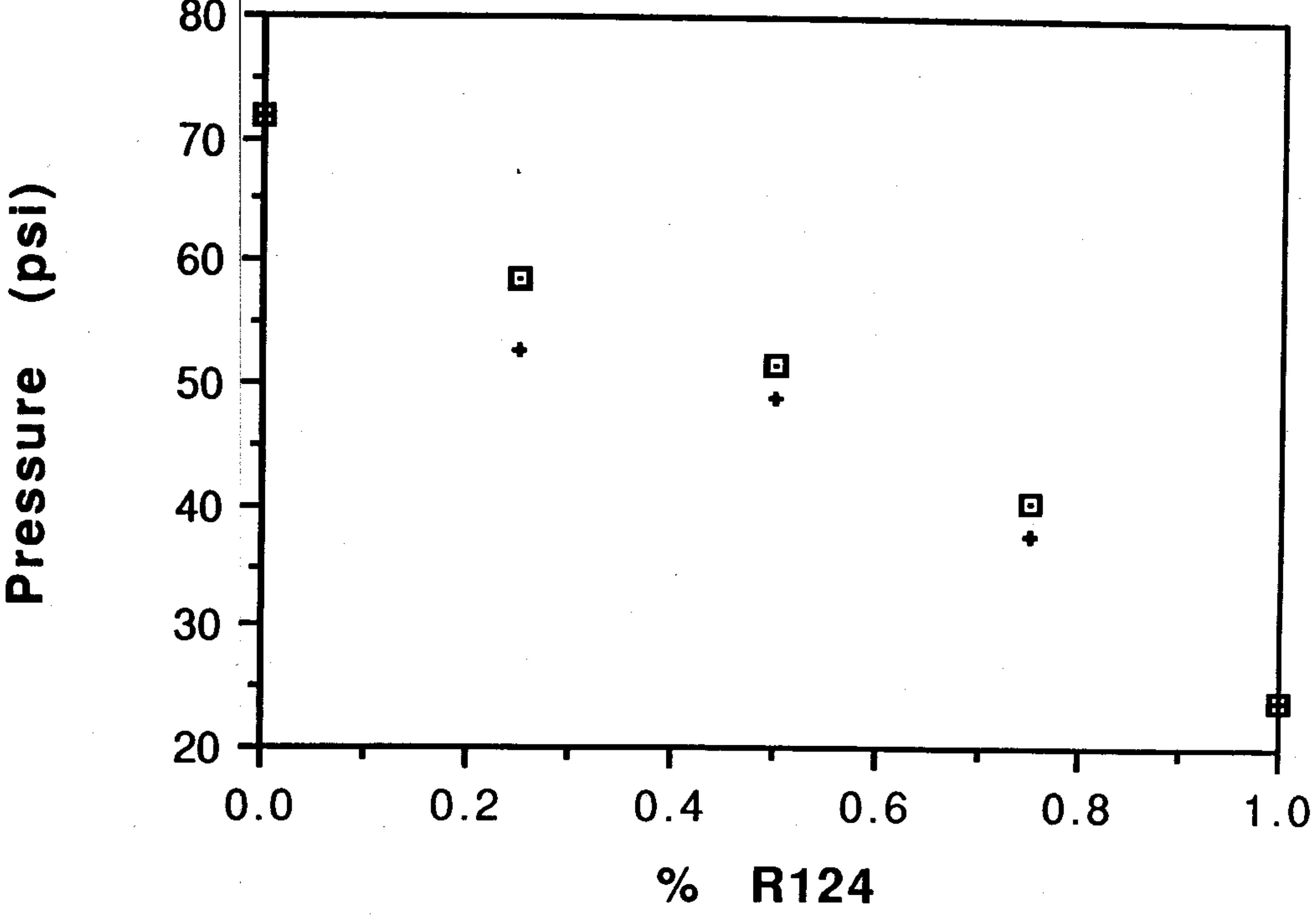


FIGURE 16 BINARY MIXTURE OF R22 + R124

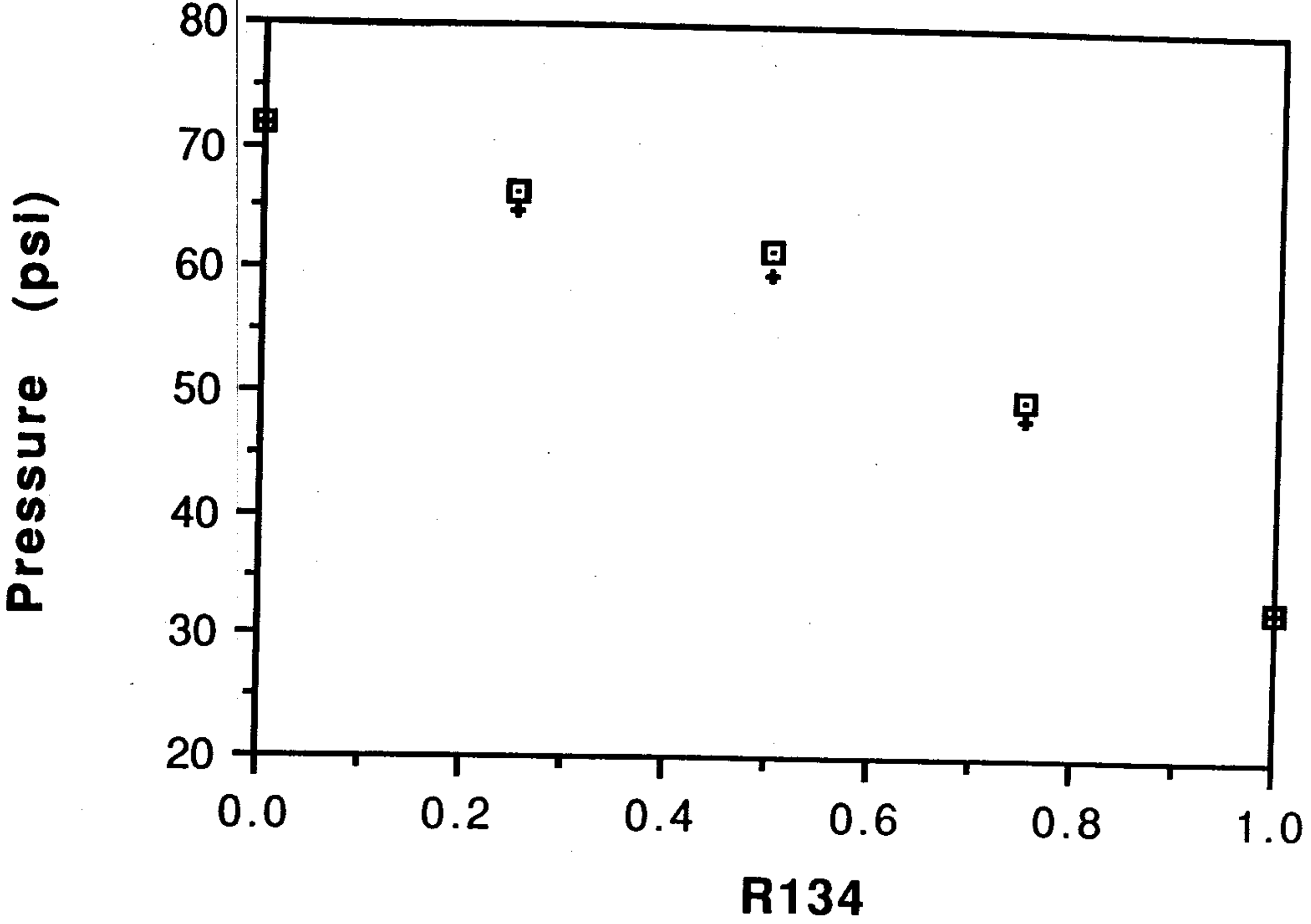


FIGURE 17 BINARY MIXTURE OF R22 + R134

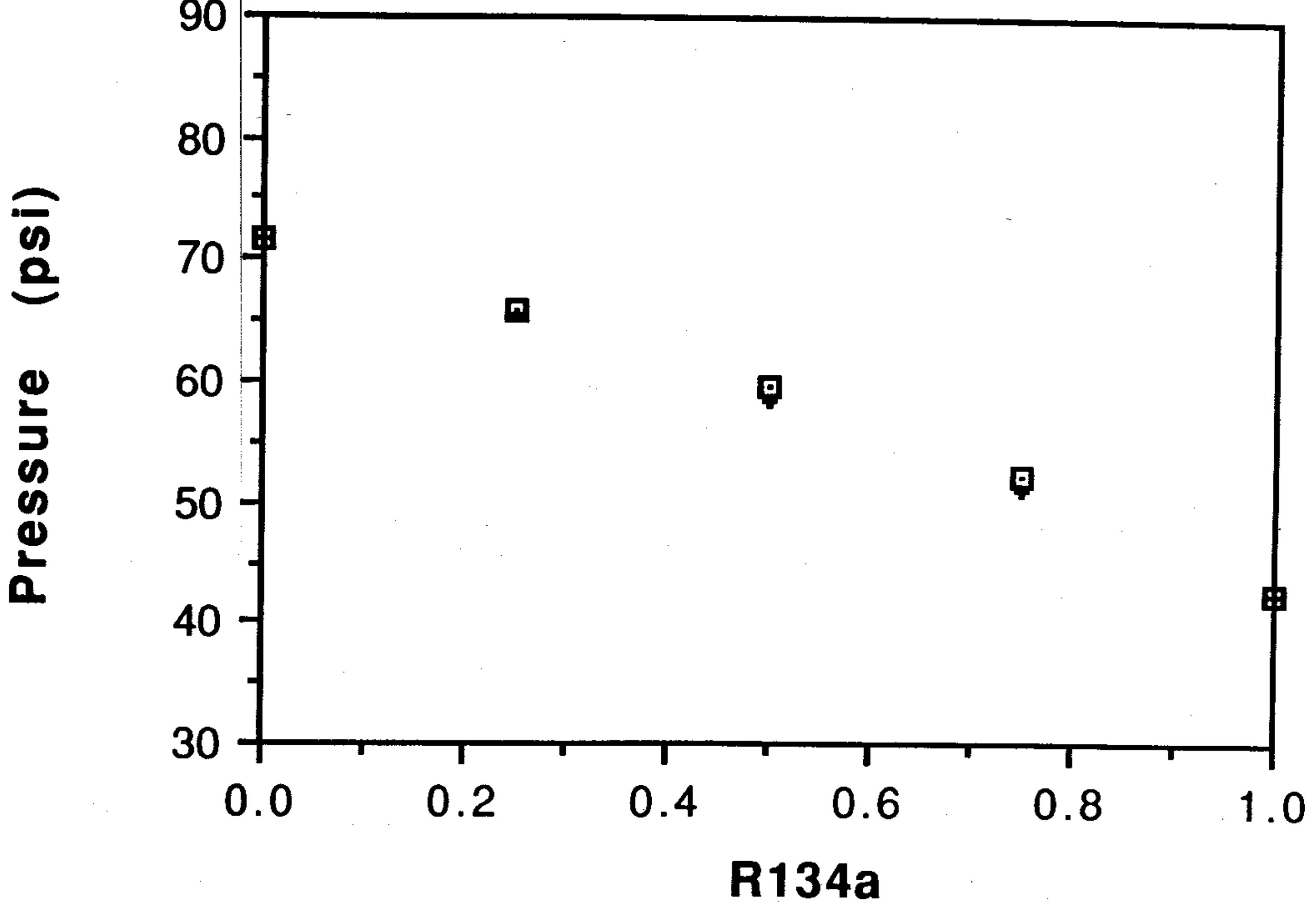


FIGURE 18 BINARY MIXTURE OF R22 + R134A

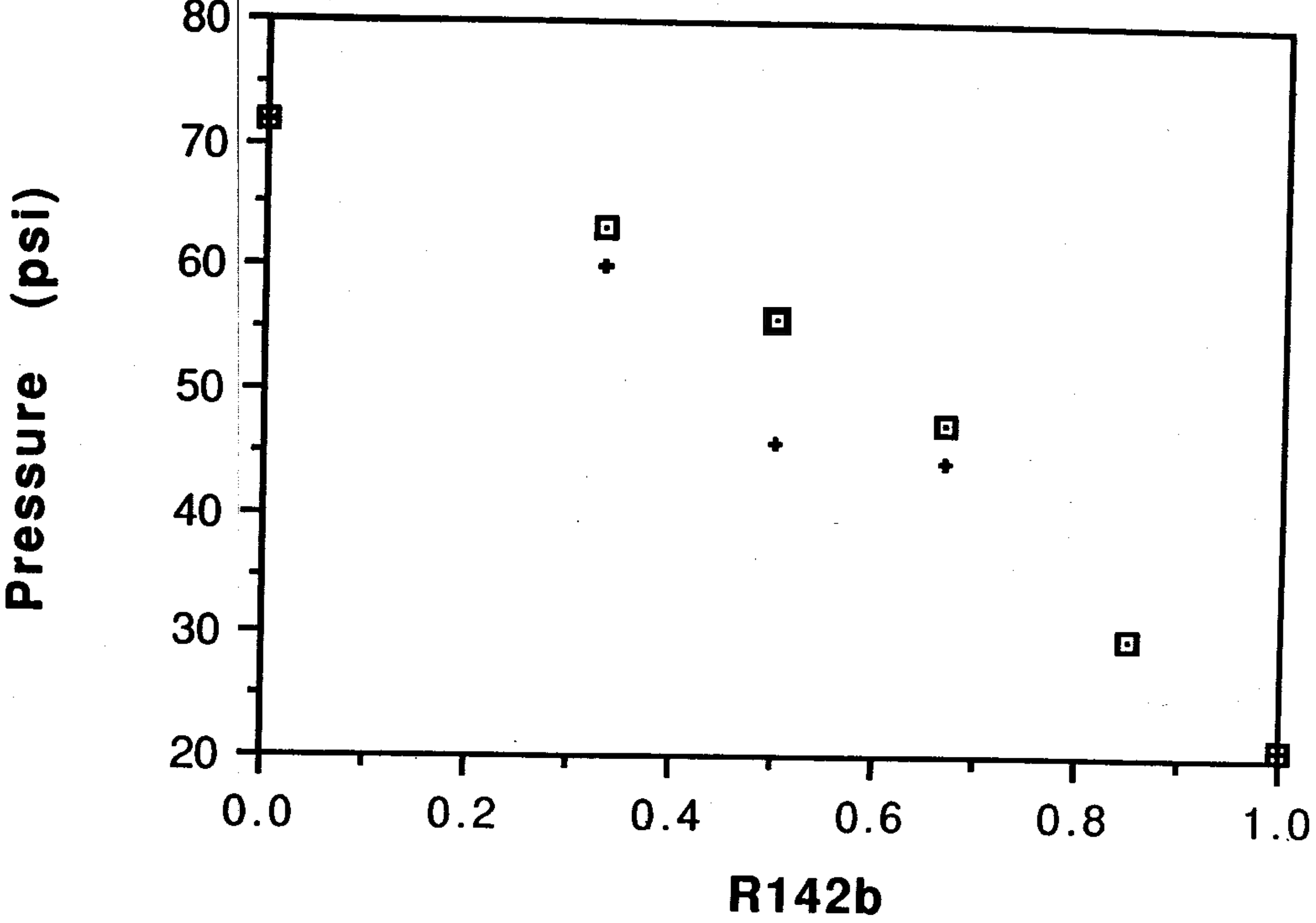


FIGURE 19 BINARY MIXTURE OF R22 + R142B

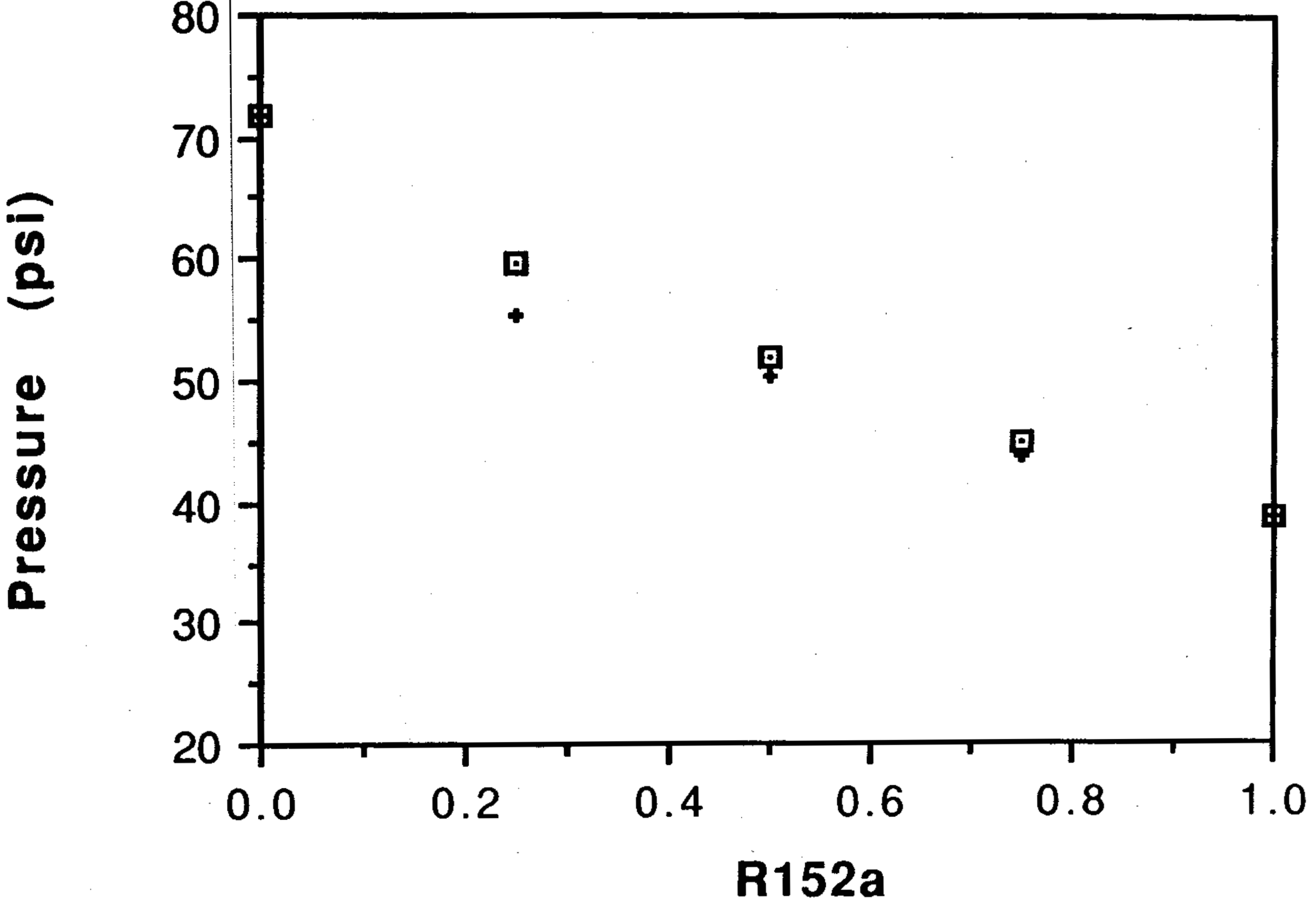
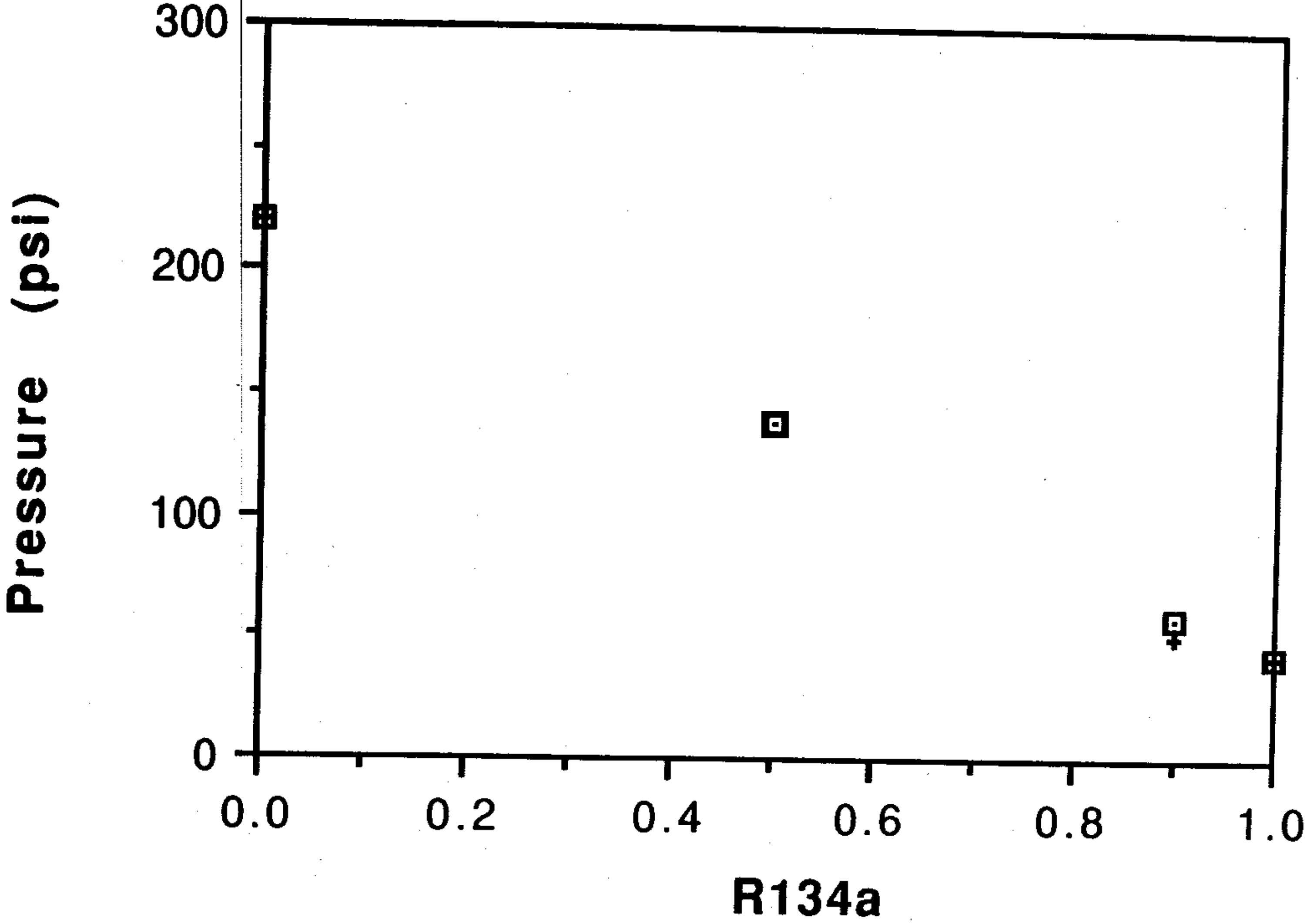


FIGURE 20 BINARY MIXTURE OF R22 + R152A



FIGUER 21 BINARY MIXTURE OF R23 + 143A

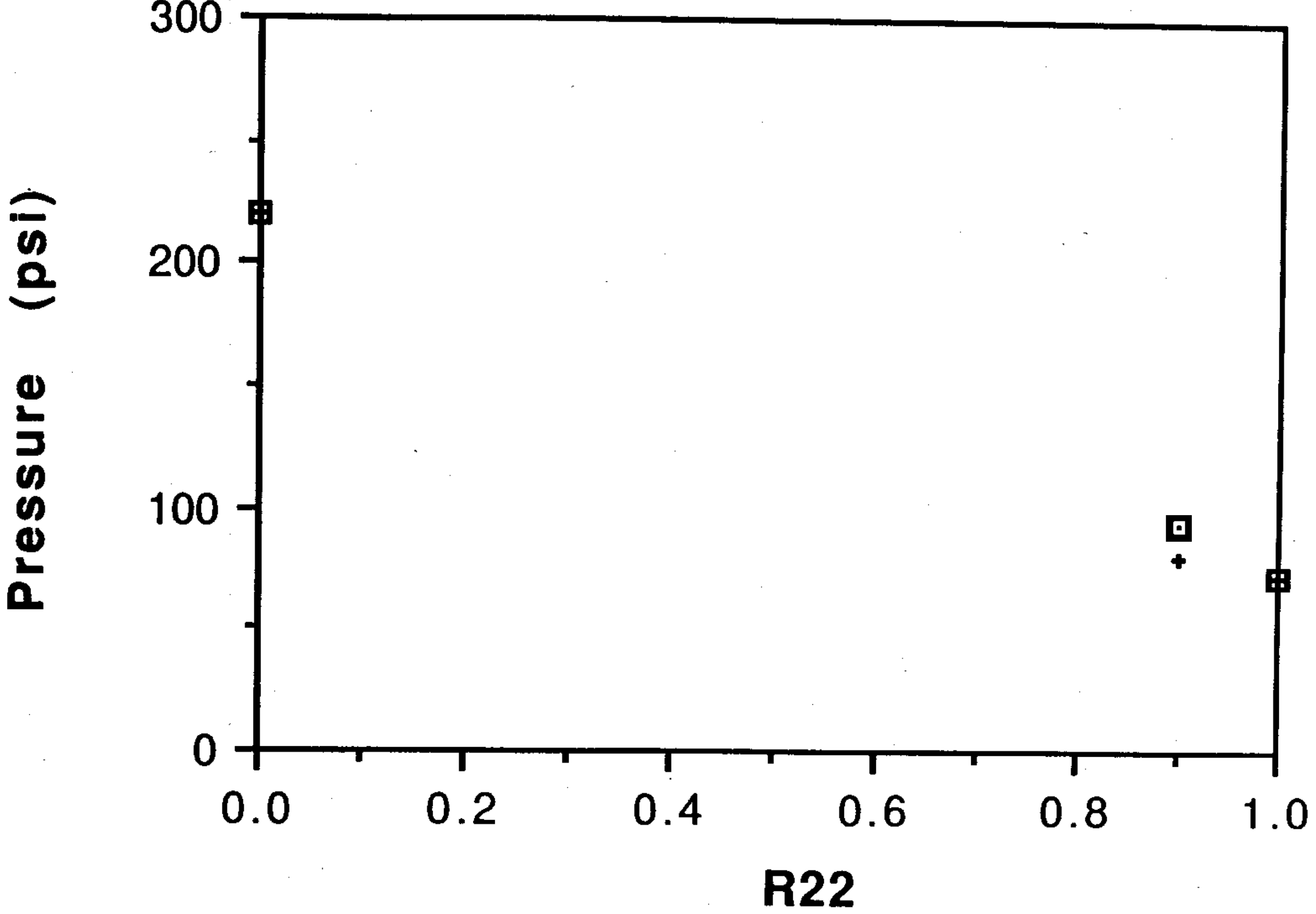


FIGURE 22 BINARY MIXTURE OF R23 + R22

FIGURE 23 **TERNARY MIXTURE OF R134A + R134 + R124**

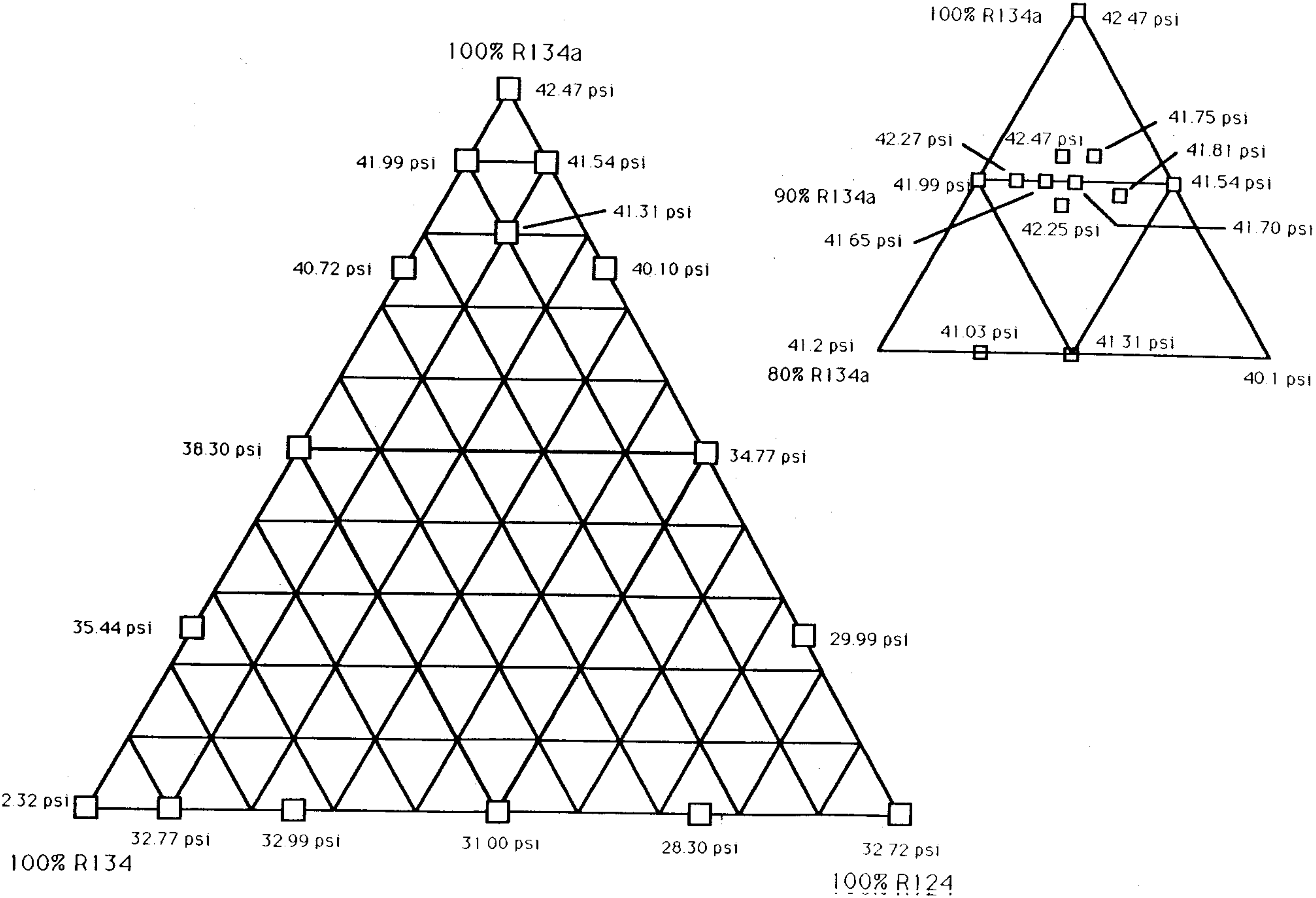


FIGURE 24 TERNARY MIXTURE OF R134A + R152A + R142B

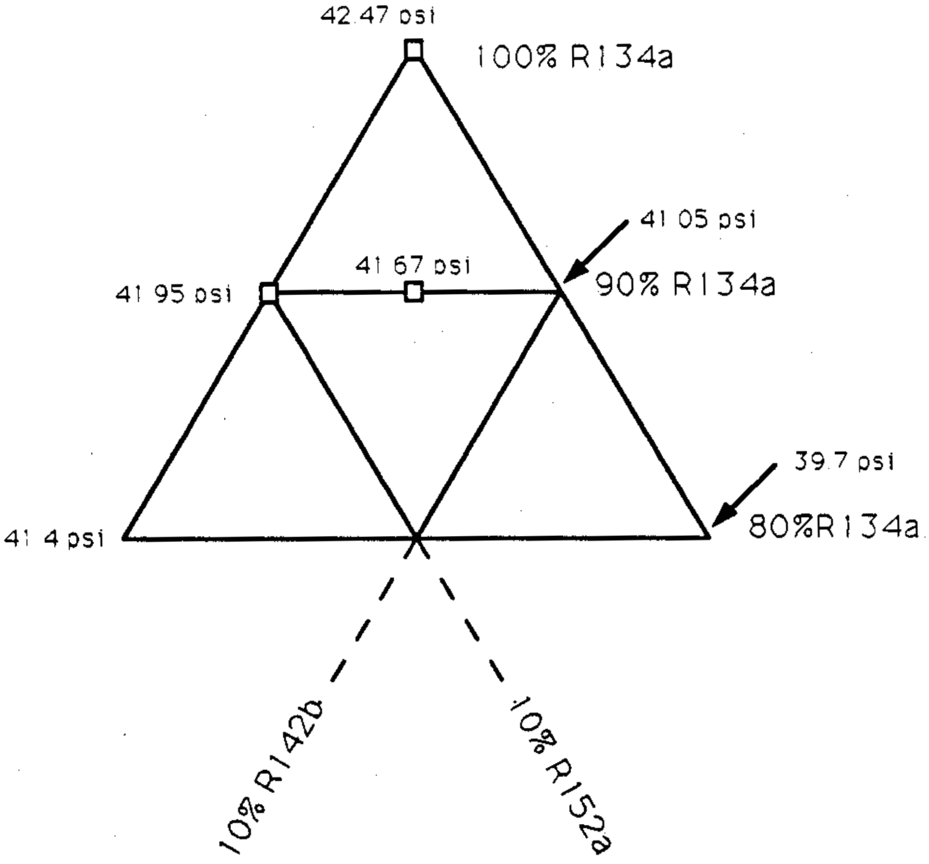


FIGURE 25 TERNARY MIXTURE OF R134A + R152A + R124

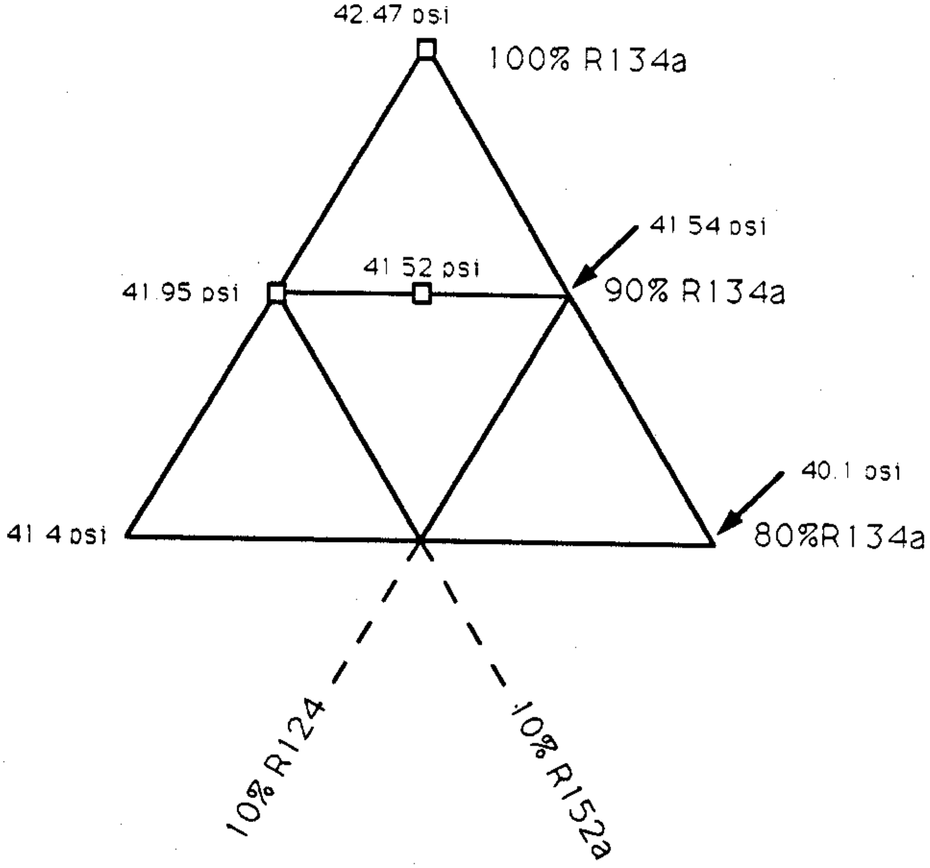


FIGURE 26 TERNARY MIXTURE OF R134A + R124 + R142B

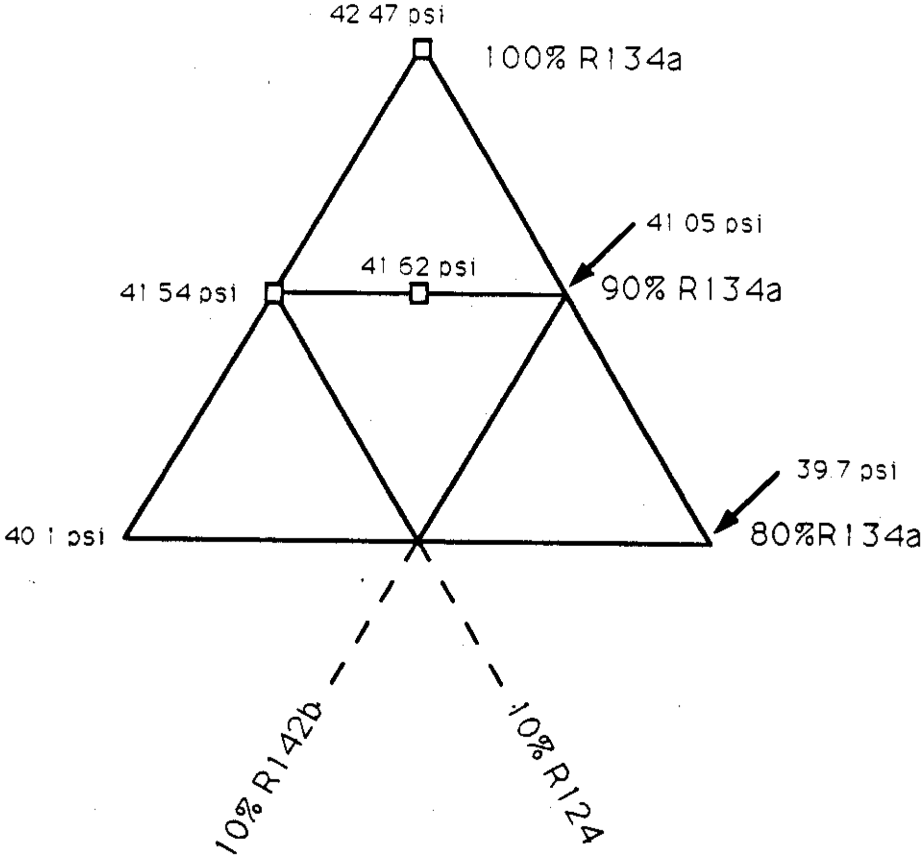
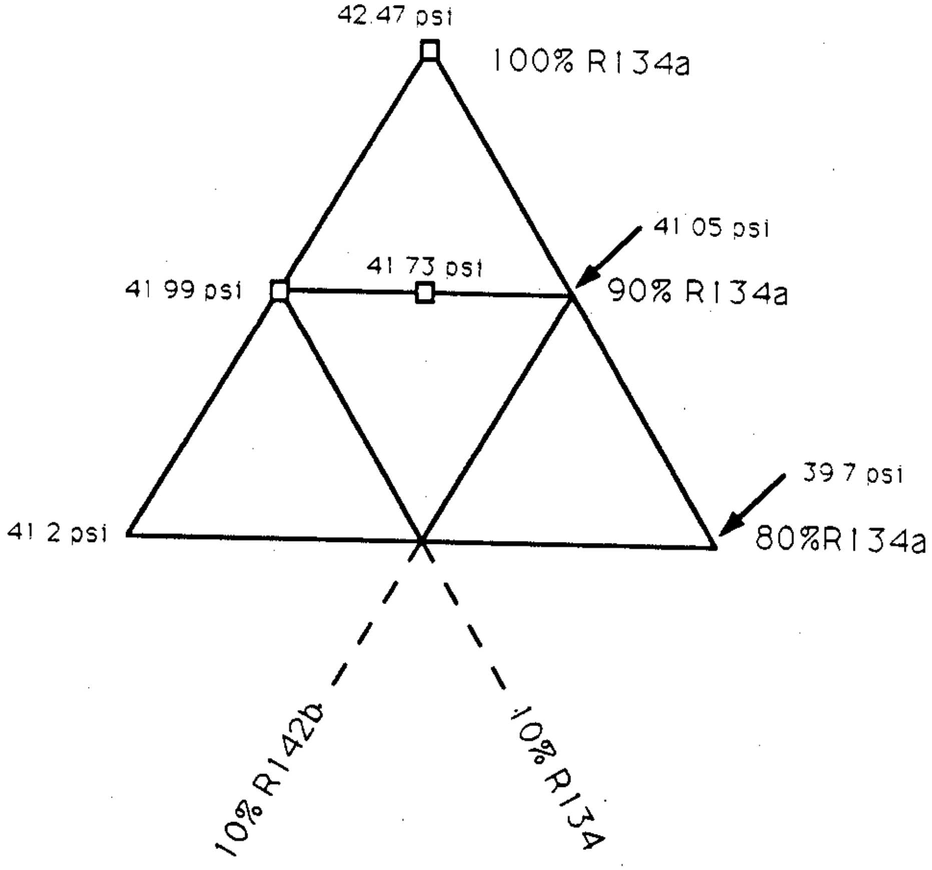


FIGURE 27 TERNARY MIXTURE OF R134A + R134 + R142B



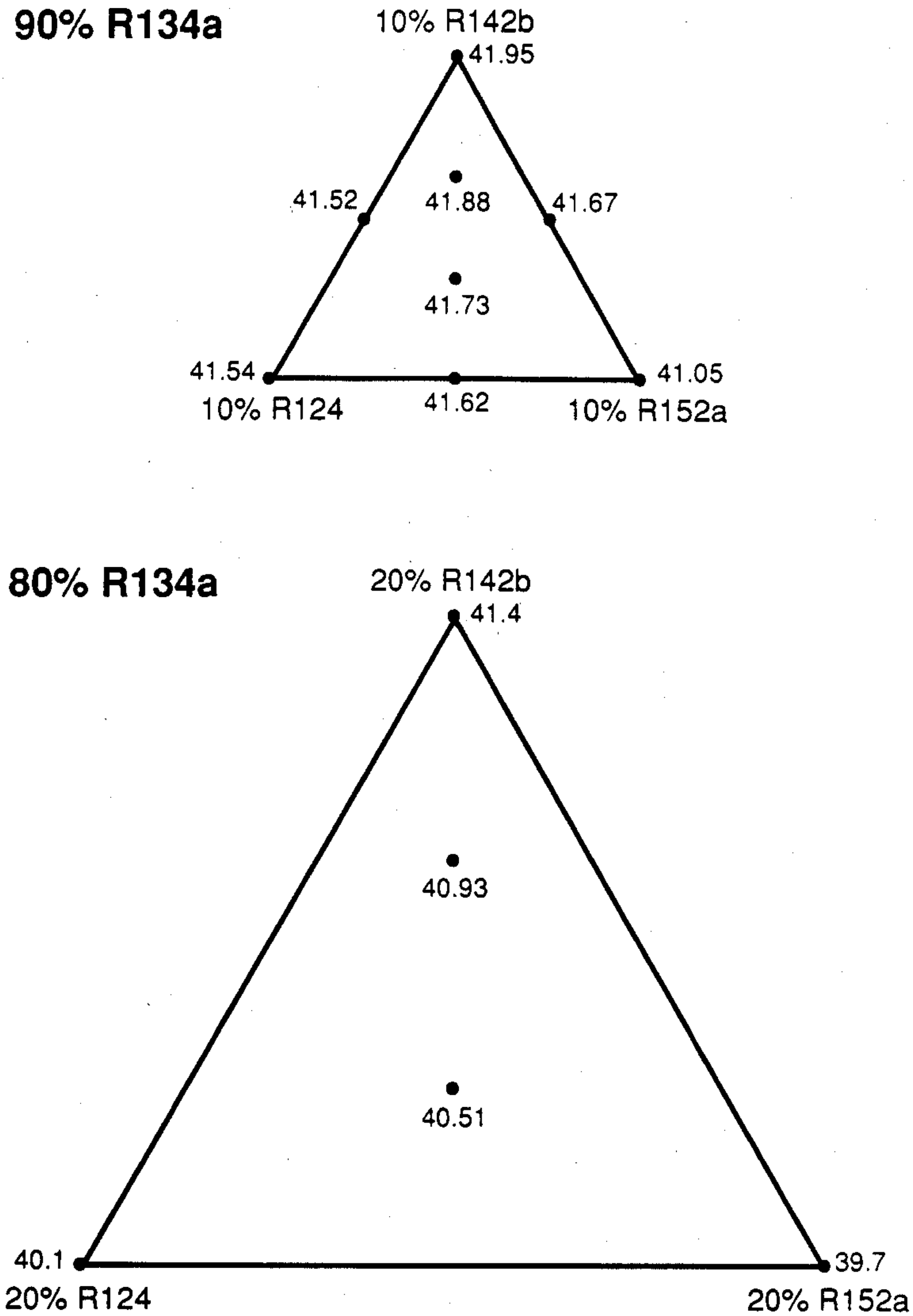


FIGURE 28 QUATERNARY MIXTURE OF R134A + R142B + R124 + R152A

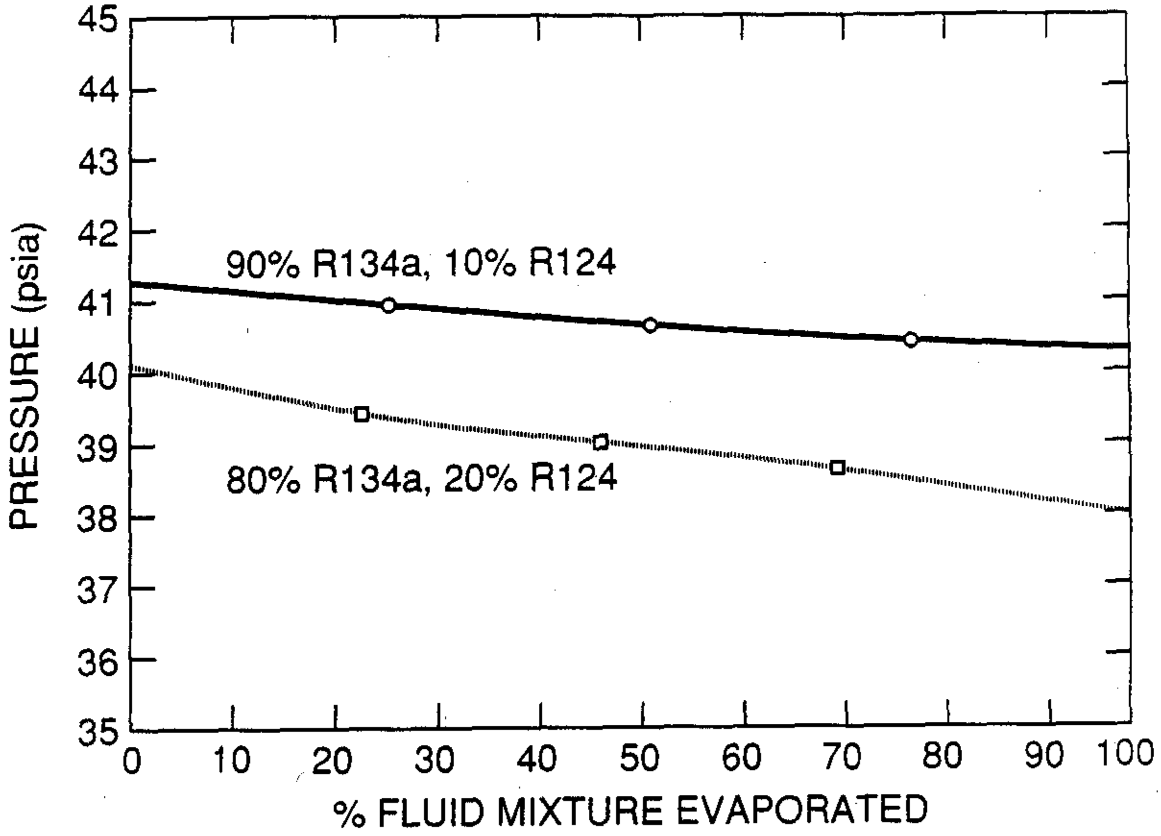


FIGURE 29 PRESSURE CHARACTERISTICS WITH LEAKAGE FOR R134A + R124