

METHOD FOR ESTIMATING MIXTURE EQUATION OF STATE PARAMETERS

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ABSTRACT

A predictive method has been developed for estimating the ζ_{ij} parameter in the mixture model of Lemmon and Jacobsen [*Int. J. Thermophysics*, **20**:1629 (1999)] applied to refrigerant mixtures. Data for 76 binary pairs were used to develop the method and these data are summarized. A wide variety of fluid properties were examined as parameters. The critical temperature, critical pressure, acentric factor, and dipole moment of each pure fluid were used in the final scheme. The values of ζ_{ij} range between -106 and $+11$; a value of zero for ζ_{ij} corresponds to a pseudo ideal mixture. This method is implemented in the NIST REFPROP database for fluids typically used as refrigerants in engineering practice, and should prove useful in the evaluation of new refrigerant blends.

1. MIXTURE MODEL

In the widely used NIST REFPROP database (Lemmon and McLinden, 2001), the Lemmon-Jacobsen (L-J) (1999) model is used to calculate the properties of mixtures of refrigerants, hydrocarbons, and cryogenics. It applies mixing rules to the reduced Helmholtz energy, α , of the components:

$$\alpha_{mix} = \sum_{j=1}^n [x_j (\alpha_j^{id} + \alpha_j^r) + x_j \ln x_j] + \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j F_{ij} \alpha_{ij}^{excess}. \quad (1)$$

The first summation represents the ideal solution when used with the appropriate reducing parameters; it consists of ideal gas (superscript *id*) and residual or real fluid (superscript *r*) terms for each of the pure fluids in the n component mixture. The $x_j \ln x_j$ terms arise from the entropy of mixing of ideal gases where x_j is the mole fraction of component j . The double summation accounts for the “excess” Helmholtz energy or “departure” from an ideal solution. The α_{ij}^{excess} is a generalized function that is applicable to broad classes of fluids and is fitted to experimental data. The F_{ij} are generalizing parameters that relate the behavior of one binary pair with that of another. The functions in Eq. (1) are evaluated at a reduced temperature τ and density δ given by:

$$\tau = \frac{T^*}{T_{mix}}, \text{ with } T^* = \sum_{i=1}^n x_i T_i^{crit} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j \zeta_{ij}, \text{ and} \quad (2)$$

$$\delta = \frac{\rho_{mix}}{\rho^*}, \text{ with } \rho^* = \left[\sum_{i=1}^n \frac{x_i}{\rho_i^{crit}} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j \xi_{ij} \right]^{-1}. \quad (3)$$

Thus, the L-J model contains one generalized function α_{ij}^{excess} and three mixture-dependent parameters F_{ij} , ζ_{ij} , and ξ_{ij} for each binary mixture. Multicomponent mixtures are modeled using only the constituent binary parameters. With this model, all of the thermodynamic properties can be calculated. Ideally F_{ij} , ζ_{ij} , and ξ_{ij} would be determined from high-quality data for each binary pair of interest. However, in cases where such data are not available, a method for predicting one or more of these parameters is needed.

The ζ_{ij} parameter is the most important of the three system-dependent parameters in the mixture model, and this single parameter captures the most essential features of refrigerant mixture behavior, including the azeotropic behavior that exists for some fluid pairs (Lemmon and Tillner-Roth, 1999). With this parameter alone, vapor-liquid equilibria for nearly all systems can be calculated with uncertainties close to that obtained by using the full model. (When using only ζ_{ij} , the parameters ξ_{ij} and F_{ij} in the L-J model are set to zero.) Due to a lack of data (published density data were available for fewer than 1/3 of the mixtures studied), it has not been possible to develop a predictive scheme for the F_{ij} and ξ_{ij} parameters; the largest influence of these parameters is in the calculation of densities.

The ζ_{ij} parameters were determined for all the systems studied in this work (including those systems for which more accurate modeling had already taken place in other work) to form a dataset that could be used to develop a predictive scheme. Various fluid-specific constants were examined in developing the predictive method; these included the dipole moment, molecular volume, acentric factor, critical temperature, critical pressure, critical density, triple point temperature, and the normal boiling point temperature. Various ways of combining the pure fluid properties were used to find a relation between these parameters and ζ_{ij} . It was necessary to determine the relationships among the various pure fluid parameters and the functional form of an equation that would allow the estimation of this mixture parameter. The relationships are neither unique nor theoretically justified. In the end, a strictly empirical relation was correlated that used the critical temperature T^{crit} , critical pressure p^{crit} , and acentric factor ω . The dipole moment μ was used to determine the order of the pure components in the equation. In this estimation scheme, ζ_{ij} is given by

$$\zeta_{ij} \frac{T_1^{crit}}{T_2^{crit}} = 40.4 - 25.03 \times 2^m, \text{ with } m = \left[\frac{T_1^{crit}}{T_2^{crit}} \frac{p_2^{crit}}{p_1^{crit}} \frac{\omega_2}{\omega_1} \right], \quad (4)$$

where fluid “1” has the smaller value of the dipole moment. In the special case where the dipole moments of the two fluids are identical, fluid “1” has the larger value of $T^{crit}/(p^{crit}\omega)$. Values of the critical parameters and acentric factors for the systems studied in this work were taken from Version 7 of the REFPROP database (Lemmon and McLinden, 2001) and are given in Table 1. A value of zero for ζ_{ij} corresponds to “ideal mixing”. Figure 1 depicts the correlation given by Eq. (4).

Table 1. Critical Parameters and Acentric Factors

Fluid	T^{crit} (K)	p^{crit} (MPa)	ω	μ (debye)	Fluid	T^{crit} (K)	p^{crit} (MPa)	ω	μ (debye)
Propane	369.825	4.2471	0.1524	0.083	R113	487.21	3.3922	0.2525	0.803
Propylene	365.57	4.6646	0.1408	0.4	R114	418.83	3.2570	0.2523	0.658
CO ₂	304.128	7.3773	0.2239	0.0	R115	353.1	3.1200	0.2520	0.52
R11	471.11	4.4076	0.1887	0.45	R116	293.03	3.0420	0.2540	0.0
R12	385.12	4.1361	0.1795	0.51	R123	456.831	3.6618	0.2819	1.356
R13	302.00	3.8790	0.1723	0.51	R124	395.425	3.6243	0.2881	1.469
R14	227.51	3.7500	0.1785	0.0	R125	339.165	3.6290	0.3061	1.563
R21	451.48	5.1812	0.2061	1.37	R134a	374.21	4.0593	0.3268	2.058
R22	369.295	4.9900	0.2208	1.458	R141b	479.96	4.4600	0.2235	2.014
R23	299.293	4.8280	0.2646	1.649	R142b	410.26	4.0700	0.2337	2.14
R32	351.255	5.7820	0.2769	1.978	R143a	345.857	3.7610	0.2615	2.34
R41	317.28	5.8970	0.2012	1.851	R152a	386.411	4.5168	0.2752	2.262

2. RESULTS AND DISCUSSION

Table 2 summarizes the experimental data used in the development of this refrigerant mixture model. Data for 76 binary pairs were used in the development of this method. About three-fourths of the binary pairs contain an HCFC and/or CFC and are not appropriate for use in modern environmentally friendly refrigeration equipment. However, the HCFC and CFC-containing mixtures have provided a wider range of molecular parameters that were useful in the development of the model. These data are reasonably complete for the mixtures examined, but not exhaustive. There are additional data for several of the mixtures marked with an asterisk that are referenced in McLinden *et al.* (1998) but which are not included here for reasons of space. A few data points have been removed from individual data sets that were either obviously in error, or for which the iterative programs used to calculate the properties failed at the given experimental conditions.

The values of ζ_{ij} determined by fitting experimental data and those calculated from Eq. (4) are given in Table 2. The overall AAD of the 4439 VLE data points analyzed is 1.77%, based on ζ_{ij} values fitted to experimental data, compared to 4.50% for ζ_{ij} values calculated with Eq. (4); the corresponding deviations for the 10373 PVT data points are 0.94% and 1.71%. The data for the 76 mixtures studied here span a wide range of quality, and the deviations include scatter and systematic deviations in the data. The deviations for some of the recently-studied HFC mixtures such as R125/143a and R134a/152a are quite good as shown in Table 2. The L-J mixture model is capable of reproducing mixture PVT data within 0.2% in density and VLE data to about 1.0% in bubble point pressure when the three parameters ζ_{ij} , ξ_{ij} , and F_{ij} are fitted to high-quality data. An additional factor in the larger deviations seen here (as compared to the three parameter model), even when ζ_{ij} values based on experimental data are used, is the compromise in accuracy in fitting a single parameter instead of three. In particular, PVT data are most sensitive to the F_{ij} parameter, so density values calculated using the single parameter model reported here show the greatest relative degradation from the optimum case. To these effects, one must add the uncertainty of the predictive scheme itself. All properties stem from molecular structure and the interactions between molecules; likewise the parameters used in the present prediction are derived from molecular structure. But the relationship in Equation (4) is empirical and does not fully capture the physics of the actual molecular interactions occurring in a mixture.

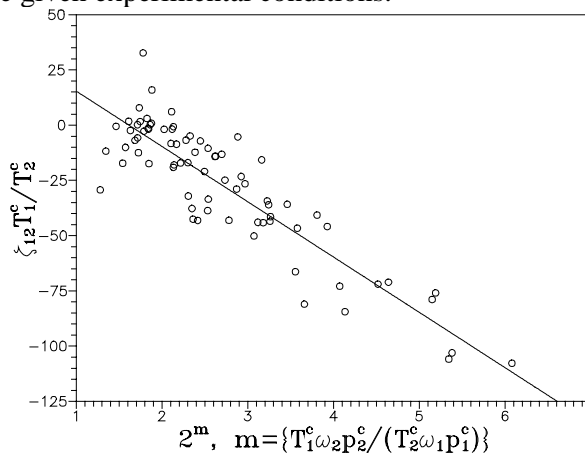


Figure 1. Comparison of ζ_{12} values derived from experimental data (circles) with those calculated from the estimation method (solid line)

3. CONCLUSIONS

A method has been developed to estimate the ζ_{ij} parameter in the Lemmon-Jacobsen mixture model. The method calculates properties with an overall average absolute deviation of 4.5% in bubble-point pressure and 1.7% in density. This new scheme does not replace the values of F_{ij} , ξ_{ij} , and ζ_{ij} determined directly for binary mixtures with extensive data, but it should prove useful in the evaluation of new refrigerant blends. The support of this work by the U.S. Department of Energy is gratefully acknowledged.

Table 2. Values of ζ_{ij} Determined from Fitting Experimental Data and Calculated from Eq. (4), and Comparisons with Experimental Data.

Binary Mixture and ζ_{ij} values					Binary Mixture and ζ_{ij} values				
Author	Data Type	# Pts.	AAD Exp.	AAD Calc.	Author	Data Type	# Pts.	AAD Exp.	AAD Calc.
propane/R22 $\zeta_{exp} = -43.44$ $\zeta_{calc} = -41.13$					CO ₂ /R41 $\zeta_{exp} = 1.79$ $\zeta_{calc} = 0.06$				
Nagahama (1986)	VLE	1	0.215	0.957	Holcomb (1998)	VLE	25	0.889	1.125
Bivens (1996)	VLE	20	0.606	1.199	Magee (1996)	PVT	214	1.559	1.370
propane/R32 $\zeta_{exp} = -102.3$ $\zeta_{calc} = -106.2$					CO ₂ /R142b $\zeta_{exp} = -15.84$ $\zeta_{calc} = 9.11$				
Holcomb (1998)	VLE	64	2.251	3.808	Lavrenchenko (1983)	VLE	17	3.511	12.94
Holcomb (1998)	PVT	49	4.067	4.133	R11/R12 $\zeta_{exp} = -0.53$ $\zeta_{calc} = -10.59$				
propane/R115 $\zeta_{exp} = -41.19$ $\zeta_{calc} = -19.15$					Loi (1983)	VLE	66	1.955	3.697
Nagahama (1986)	VLE	1	0.405	10.85	Kruse (1977)	PVT	6	4.214	4.266
propane/R125 $\zeta_{exp} = -74.31$ $\zeta_{calc} = -46.94$					Ström (1990)	PVT	66	0.387	0.425
Holcomb (1998)	VLE	48	1.883	9.798	R11/R13 $\zeta_{exp} = -7.87$ $\zeta_{calc} = -12.36$				
Bivens (1996)	VLE	17	1.337	9.892	Kriebel (1966)	VLE	130	2.222	3.708
Holcomb (1998)	PVT	26	1.849	6.662	R11/R22 $\zeta_{exp} = -26.89$ $\zeta_{calc} = -31.64$				
propane/R134a $\zeta_{exp} = -73.73$ $\zeta_{calc} = -62.24$					Meskel (1982a)	VLE	29	0.871	2.250
Holcomb (1998)	VLE	60	1.396	5.153	R11/R23 $\zeta_{exp} = -67.26$ $\zeta_{calc} = -59.30$				
Kleiber (1994)	VLE	23	2.163	7.116	Chareton (1990)	VLE	11	5.111	6.158
Holcomb (1998)	PVT	49	2.345	5.759	R12/R13 $\zeta_{exp} = -13.44$ $\zeta_{calc} = -11.82$				
propylene/R12 $\zeta_{exp} = -8.75$ $\zeta_{calc} = -12.92$					Agarwal (1980)	VLE	118	3.837	4.280
Kleiber (1994)	VLE	42	0.259	1.659	Mollerup (1976)	VLE	17	1.033	1.167
propylene/R13 $\zeta_{exp} = -31.18$ $\zeta_{calc} = -15.19$					R12/R22 $\zeta_{exp} = -22.32$ $\zeta_{calc} = -31.43$				
Kleiber (1994)	VLE	16	0.587	6.960	Eiseman (1957)	VLE	21	3.286	1.185
propylene/R22 $\zeta_{exp} = -15.86$ $\zeta_{calc} = -39.13$					Kriebel (1967)	VLE	166	1.170	3.675
Kleiber (1994)	VLE	35	0.118	10.25	Löffler (1960)	VLE	126	1.889	2.817
propylene/R23 $\zeta_{exp} = -62.15$ $\zeta_{calc} = -73.29$					Pennington (1957)	VLE	10	0.851	2.127
Kleiber (1994)	VLE	13	2.418	8.522	Spauschus (1962)	VLE	70	1.222	1.570
propylene/R114 $\zeta_{exp} = -21.87$ $\zeta_{calc} = -14.85$					Ström (1989)	VLE	16	2.779	1.767
Kleiber (1994)	VLE	14	2.305	3.943	White (1959)	VLE	41	2.536	6.258
propylene/R115 $\zeta_{exp} = -41.09$ $\zeta_{calc} = -18.06$					Yin (1986)	PVT	12	0.780	1.090
Kleiber (1994)	VLE	19	1.606	8.490	Takaishi (1982)	PVT	297	1.363	3.812
propylene/R134a $\zeta_{exp} = -46.98$ $\zeta_{calc} = -59.25$					White (1959)	PVT	53	0.417	1.589
Kleiber (1994)	VLE	23	2.083	5.642	R12/R23 $\zeta_{exp} = -55.24$ $\zeta_{calc} = -58.86$				
propylene/R142b $\zeta_{exp} = -8.04$ $\zeta_{calc} = -23.37$					Geller (1972)	VLE	36	4.699	5.115
Kleiber (1994)	VLE	23	1.265	7.716	R12/R32 $\zeta_{exp} = -71.97$ $\zeta_{calc} = -80.71$				
propylene/R152a $\zeta_{exp} = -37.88$ $\zeta_{calc} = -48.82$					Kang (1996a)	VLE	14	0.433	3.175
Ohgaki (1990)	VLE	18	2.787	1.648	R12/R113 $\zeta_{exp} = 20.16$ $\zeta_{calc} = -8.47$				
Kleiber (1994)	VLE	28	1.539	4.502	Hackstein (1976)	VLE	46	8.335	12.92
CO ₂ /R12 [†] $\zeta_{exp} = -37.06$ $\zeta_{calc} = 10.62$					R12/R114 $\zeta_{exp} = -2.04$ $\zeta_{calc} = -11.18$				
Lavrenchenko (1983)	VLE	25	3.421	16.41	Kruse (1985)	VLE	39	0.872	4.239
CO ₂ /R22 $\zeta_{exp} = -0.62$ $\zeta_{calc} = 4.58$					Kubota (1990)	VLE	25	1.986	2.203
Nohka (1973)	VLE	40	2.955	4.795	Ström (1989)	VLE	34	2.376	4.163
Roth (1992)	VLE	52	2.002	3.684	Ström (1990)	PVT	33	0.626	0.877
Wang (1991)	VLE	71	1.587	1.244	R12/R134a $\zeta_{exp} = -45.30$ $\zeta_{calc} = -47.75$				
CO ₂ /R23 $\zeta_{exp} = -12.26$ $\zeta_{calc} = -2.71$					Kleiber (1994)	VLE	24	0.808	1.466
Roth (1992)	VLE	41	0.675	3.094	R12/R142b $\zeta_{exp} = -18.1$ $\zeta_{calc} = -18.33$				
CO ₂ /R32 $\zeta_{exp} = -3.12$ $\zeta_{calc} = -5.06$					Lavrenchenko (1983)	VLE	16	1.424	1.448
Adams (1971)	VLE	48	1.109	1.631					

Table 2. (Continued)

Binary Mixture and ζ_{ij} values					Binary Mixture and ζ_{ij} values				
Author	Data Type	# Pts.	AAD Exp.	AAD Calc.	Author	Data Type	# Pts.	AAD Exp.	AAD Calc.
R12/R143a $\zeta_{exp} = -38.69$ $\zeta_{calc} = -26.21$					Hinrichsen (1969)	VLE	62	1.144	7.734
Geller (1972)	VLE	48	2.787	6.021	Hongo (1990)	VLE	66	1.466	4.040
R12/R152a $\zeta_{exp} = -44.30$ $\zeta_{calc} = -39.31$					Kimura (1981)	VLE	20	1.049	5.703
Pennington (1950)	VLE	17	0.838	1.787	Nagahama (1986)	VLE	1	0.281	7.730
Sand (1994)	VLE	6	2.080	1.186	Kimura (1981)	PVT	147	0.717	4.308
Sinka (1967)	VLE	11	0.382	2.159	Martin (1970)	PVT	61	1.487	7.610
Wright (1985)	VLE	17	0.837	1.785	R22/R124 $\zeta_{exp} = -2.95$ $\zeta_{calc} = -6.24$				
Sinka (1967)	PVT	28	3.406	5.491	Sand (1994)	VLE	3	8.037	7.091
R13/R14 $\zeta_{exp} = -9.08$ $\zeta_{calc} = -2.34$					R22/R125 $\zeta_{exp} = -16.52$ $\zeta_{calc} = -12.10$				
Proust (1979)	VLE	10	0.510	4.672	Bivens (1996)	VLE	20	0.335	1.657
Kubic (1981)	VLE	58	0.944	3.581	R22/R134a $\zeta_{exp} = -6.89$ $\zeta_{calc} = -16.86$				
Zakharov (1977)	VLE	15	1.834	5.159	Arita (1991)	VLE	14	0.367	4.435
R13/R23 $\zeta_{exp} = -40.35$ $\zeta_{calc} = -54.40$					Nishiumi (1990)	VLE	26	1.366	1.885
Sinka (1970)	VLE	9	1.143	7.223	Nishiumi (1993)	VLE	53	0.360	3.681
Stein (1971)	VLE	65	1.376	6.149	Sand (1994)	VLE	3	1.098	4.462
Tanishita (1972)	VLE	8	1.239	8.658	R22/R142b $\zeta_{exp} = 0.23$ $\zeta_{calc} = -2.77$				
Oguchi (1973)	PVT	169	2.121	4.911	Maezawa (1992)	VLE	45	0.864	1.572
Sinka (1970)	PVT	33	1.545	4.573	Sousa (1992)	PVT	73	0.476	0.649
R13/R113 $\zeta_{exp} = 12.71$ $\zeta_{calc} = -4.86$					Dressner (1993)	PVT	109	0.316	0.518
Meskel (1982b)	VLE	47	1.337	9.836	Xu (1989)	PVT	89	3.151	3.030
R14/R23 $\zeta_{exp} = -32.70$ $\zeta_{calc} = -36.86$					Kumagai (1991)	PVT	250	2.131	3.100
Piacentini (1967)	VLE	87	4.677	5.969	Ström (1993)	PVT	48	0.472	0.590
Lange (1970)	PVT	141	0.870	0.703	R22/R152a $\zeta_{exp} = 7.42$ $\zeta_{calc} = -13.03$				
R21/R114 $\zeta_{exp} = -34.61$ $\zeta_{calc} = -18.67$					Larue (1990)	VLE	28	0.788	11.79
Hinrichsen (1969)	VLE	76	1.047	6.722	Maezawa (1991a)	VLE	64	3.933	6.435
R22/R23 $\zeta_{exp} = -10.68$ $\zeta_{calc} = -21.94$					Sand (1994)	VLE	3	2.386	12.69
Laugier (1994)	VLE	17	2.130	2.860	Dressner (1993)	PVT	142	0.197	2.350
Roth (1992)	VLE	45	0.707	3.991	Ström (1993)	PVT	64	0.563	1.332
Sand (1994)	VLE	1	6.599	13.90	R23/R113 $\zeta_{exp} = -63.32$ $\zeta_{calc} = -57.92$				
R22/R32 $\zeta_{exp} = -5.05$ $\zeta_{calc} = -30.22$					Valtz (1987)	VLE	14	14.84	12.98
Kang (1996a)	VLE	11	0.264	10.88	R23/R114 $\zeta_{exp} = -51.4$ $\zeta_{calc} = -51.93$				
R22/R113 $\zeta_{exp} = -27.29$ $\zeta_{calc} = -30.89$					Laugier (1994)	VLE	12	7.278	7.391
Valtz (1986)	VLE	11	3.065	4.097	R23/R116 $\zeta_{exp} = -51.22$ $\zeta_{calc} = -37.25$				
R22/R114 $\zeta_{exp} = -25.51$ $\zeta_{calc} = -27.70$					Bivens (1996)	VLE	33	1.361	8.296
Fukuizumi (1991a)	VLE	27	1.073	1.173	R23/R134a [†] $\zeta_{exp} = 40.90$ $\zeta_{calc} = -5.14$				
Hasegawa (1985)	VLE	30	2.674	2.477	Sand (1994)	VLE	2	7.089	30.69
Kruse (1985)	VLE	36	4.265	3.508	R32/R115 $\zeta_{exp} = -83.98$ $\zeta_{calc} = -62.71$				
Kruse (1989)	VLE	47	1.003	1.376	Mears (1968)	VLE	19	1.121	9.167
Kubota (1990)	VLE	44	3.629	2.918	Mears (1968)	PVT	119	5.427	14.89
Mishima (1993)	VLE	43	2.946	3.269	R32/R125* $\zeta_{exp} = -14.54$ $\zeta_{calc} = -26.18$				
Ström (1989)	VLE	13	5.415	5.002	Defibaugh (1995)	VLE	10	0.763	3.620
Fukuizumi (1991b)	PVT	264	0.631	0.777	Kleemiss (1997)	VLE	23	1.110	7.322
Hasegawa (1985)	PVT	164	0.793	1.060	Nagel (1995)	VLE	34	1.497	5.691
Kruse (1989)	PVT	97	0.765	0.824	Piao (1996)	VLE	10	0.672	5.455
Ström (1990)	PVT	33	0.538	0.566	Kleemiss (1997)	PVT	415	0.689	1.059
R22/R115 $\zeta_{exp} = -40.47$ $\zeta_{calc} = -24.01$					Magee (2000)	PVT	228	0.638	1.290
Martin (1970)	VLE	46	1.795	10.10	Piao (1996)	PVT	532	1.398	0.974

Table 2. (Continued)

Binary Mixture and ζ_{ij} values					Binary Mixture and ζ_{ij} values				
Author	Data Type	# Pts.	AAD Exp.	AAD Calc.	Author	Data Type	# Pts.	AAD Exp.	AAD Calc.
Sato (1996)	PVT	156	0.657	0.216	Sand (1994)	VLE	3	3.431	0.178
Zhang (1996)	PVT	124	0.611	0.166	R124/R152a $\zeta_{exp} = -10.33$ $\zeta_{calc} = -17.43$				
R32/R134a* $\zeta_{exp} = -6.14$ $\zeta_{calc} = -2.68$					Sand (1994)	VLE	3	2.437	6.020
Defibaugh (1995)	VLE	25	0.286	1.905	R125/R134a* $\zeta_{exp} = -2.00$ $\zeta_{calc} = -13.90$				
Kleemiss (1997)	VLE	16	0.361	1.833	Kleemiss (1997)	VLE	24	0.777	7.887
Nagel (1995)	VLE	50	0.826	1.689	Nagel (1995)	VLE	31	0.647	6.652
Piao (1996)	VLE	10	0.925	0.703	Holcomb (1998)	PVT	17	0.277	1.485
Kleemiss (1997)	PVT	390	0.417	0.403	Kleemiss (1997)	PVT	407	0.114	1.197
Magee (2000)	PVT	461	0.498	0.627	Magee (2000)	PVT	268	0.176	2.469
Piao (1996)	PVT	633	0.833	1.682	R125/R143a* $\zeta_{exp} = 3.06$ $\zeta_{calc} = -5.39$				
Sato (1994)	PVT	214	0.316	0.549	Bivens (1996)	VLE	32	0.520	3.762
R32/R143a $\zeta_{exp} = -17.00$ $\zeta_{calc} = 1.80$					Kleemiss (1997)	VLE	16	0.929	5.618
Fujiwara (1992)	VLE	6	1.587	6.919	Nagel (1995)	VLE	19	1.067	5.800
Holcomb (1998)	VLE	19	0.622	7.548	Kleemiss (1997)	PVT	151	0.043	0.951
Holcomb (1998)	PVT	43	0.884	4.129	Magee (2000)	PVT	281	0.084	1.100
R32/R152a $\zeta_{exp} = -2.64$ $\zeta_{calc} = -0.47$					R134a/R141b $\zeta_{exp} = -32.3$ $\zeta_{calc} = -32.21$				
Defibaugh (1995)	VLE	26	0.616	1.543	Zheng (1990)	VLE	38	2.599	2.626
Fujiwara (1992)	VLE	6	3.195	2.198	R134a/R142b $\zeta_{exp} = -11.07$ $\zeta_{calc} = 1.11$				
R113/R114 $\zeta_{exp} = 0.24$ $\zeta_{calc} = -7.19$					Sand (1994)	VLE	7	4.331	9.483
Lee (1988)	VLE	17	1.580	4.846	Kleiber (1994)	VLE	26	0.601	5.457
R113/R142b $\zeta_{exp} = -17.64$ $\zeta_{calc} = -18.56$					R134a/R143a* $\zeta_{exp} = 1.52$ $\zeta_{calc} = -3.00$				
Laugier (1994)	VLE	12	0.653	0.903	Bivens (1996)	VLE	35	0.409	2.179
R113/R152a $\zeta_{exp} = -52.63$ $\zeta_{calc} = -38.53$					Kleemiss (1997)	VLE	18	0.273	2.706
Valtz (1987)	VLE	12	2.252	6.650	Nagel (1995)	VLE	12	0.352	2.327
R114/R115 $\zeta_{exp} = -2.15$ $\zeta_{calc} = -6.76$					Holcomb (1998)	PVT	14	0.455	0.580
Yada (1990)	VLE	26	2.265	2.349	Kleemiss (1997)	PVT	377	0.113	0.517
Yada (1989)	PVT	239	1.206	2.497	R134a/R152a* $\zeta_{exp} = 0.87$ $\zeta_{calc} = -6.76$				
R114/R152a $\zeta_{exp} = -40.56$ $\zeta_{calc} = -34.68$					Defibaugh (1995)	VLE	13	0.279	2.773
Yada (1988)	VLE	34	2.863	3.919	Kleiber (1994)	VLE	19	0.375	3.868
Yada (1988)	PVT	306	6.186	7.916	Tillner-Roth (1993)	VLE	23	0.276	3.012
R116/R134a $\zeta_{exp} = -42.80$ $\zeta_{calc} = -29.57$					Dressner (1993)	PVT	139	0.423	1.068
Kleiber (1994)	VLE	14	3.926	10.94	Tillner-Roth (1993)	PVT	1678	0.395	0.595
R123/R134a $\zeta_{exp} = -21.73$ $\zeta_{calc} = -27.73$					R141b/R142b $\zeta_{exp} = -7.38$ $\zeta_{calc} = -11.85$				
Kubota (1991)	VLE	31	2.065	4.286	Kang (1996b)	VLE	11	0.593	2.319
R124/R134a $\zeta_{exp} = -9.93$ $\zeta_{calc} = -21.84$					R142b/R152a $\zeta_{exp} = -13.37$ $\zeta_{calc} = -23.63$				
Lee (1996)	VLE	17	0.643	5.350	Maewawa (1991b)	VLE	48	2.127	4.775
Sand (1994)	VLE	6	0.698	4.328	Sand (1994)	VLE	3	1.110	6.488
R124/R142b $\zeta_{exp} = 1.89$ $\zeta_{calc} = -5.81$					OVERALL	VLE	4439	1.771	4.501
Lee (1996)	VLE	19	0.289	2.725	OVERALL	PVT	10373	0.944	1.707

Legend: Data Type - density (PVT) or vapor liquid equilibrium (VLE), AAD Exp. – average absolute deviation between the experimental data and the model using the listed ζ_{ij} values fitted to the experimental data, AAD Calc. – average absolute deviation between the experimental data and the model using the ζ_{ij} values calculated from Eq. (4).

* Additional sources of data exist for this refrigerant mixture; see McLinden *et al.* (1998).

† The experimental data for R23/134a and CO₂/R12 are questionable, and the calculated value for ζ_{ij} is recommended in preference to the experimental value.

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