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Vapour–liquid equilibria of binary mixtures containing Stockmayer molecules

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Abstract. Using Gibbs ensemble Monte Carlo simulations, we investigated the vapour–liquid equilibria of a number of binary mixtures, some containing Lennard-Jones (LJ) and Stockmayer (SM) components, and others containing two SM components with different reduced dipole moments. Our results show that the phase coexistence properties of the mixtures are sensitive to the difference between the reduced dipole moments of the two components: an increase in this difference causes the phase envelope to widen for both the LJ–SM and SM–SM mixtures. Comparison of our results to vapour–liquid equilibria data simulated using an angle-averaged approximation of the long-range dipolar interaction, the Keesom potential, suggests that the Keesom potential is not suitable to approximate the dipolar interactions for mixtures when the dipolar interaction is dominant.

1. Introduction

An understanding of the properties of fluid mixtures containing one or more polar components is a vital issue in a number of fields, including chemical engineering and the environmental sciences. At present, the thermodynamic and phase behaviour of such fluids is not well understood in terms of molecular interactions; however, with the recent application of the Gibbs ensemble Monte Carlo (GEMC) method [1–6], the vapour–liquid equilibria (VLE) of pure Stockmayer fluids have been studied extensively. The Stockmayer (SM) potential, which represents the molecular interaction by adding an embedded point dipole to the Lennard-Jones (LJ) potential, provides a convenient model for study of polar substances. The VLE data of pure SM fluids with varying degrees of polarity have been reported by Smit *et al* [1], van Leeuwen *et al* [2], and van Leeuwen [3]. Van Leeuwen also analysed the critical data from GEMC simulations of SM fluids at various dipole moments to discuss the deviation from corresponding-states behaviour for polar fluids [3], and suggested a way to determine the SM potential parameters from VLE data for polar substances [4].

Studies of mixtures containing polar components by computer simulation have calculated the free energy of mixing and examined the local compositions of LJ–SM mixtures [7–9]. The results of de Leeuw *et al* [7] show that demixing occurs at a liquid density if the reduced dipole moment of the SM molecules becomes greater than two for an LJ–SM system. Although direct simulations of the VLE for nonpolar LJ–LJ mixtures have been

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used extensively in the past few years [10–14], direct simulations of the VLE for LJ–SM or SM–SM mixtures have not been performed: to our knowledge, the only work related to this study is from a recent paper of Sadus [15], in which the orientation-related long-range interaction between two dipoles is angle averaged, leading to the short-ranged Keesom potential [16].

In this paper, we report our GEMC simulation results of the VLE of both LJ–SM and SM–SM binary mixtures. The paper is organized as follows. In section 2, we describe the potential model and the simulation details. In section 3, we present the simulation results and show the influence of the dipolar interaction in phase diagrams for both the LJ–SM and SM–SM mixtures. We also make a comparison of our results to those of Sadus [15], who used the Keesom potential to approximate the dipole–dipole interaction, and examine the validity of the Keesom approximation for the mixtures. Our conclusions are given in section 4.

2. The potential model and the simulation method

The Stockmayer potential can be written as

$$U(\mathbf{r}_{ij}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_j) = 4\varepsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6] + \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j/r_{ij}^3 - 3(\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij})/r_{ij}^5$$

where r_{ij} is the distance between particles i and j ; σ_{ij} and ε_{ij} are the LJ size and energy parameters, respectively; and $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_j$ are the dipole moments of particles i and j respectively. The first part of the equation is the LJ potential; the rest is the interaction energy between two dipoles.

We used the NPT–Gibbs ensemble Monte Carlo technique in the simulations. The technique was developed by Panagiotopoulos *et al* [10, 17] and has become a popular method for simulating the phase equilibrium properties of fluids. In a GEMC simulation, two homogeneous phases at thermodynamic equilibrium are simulated simultaneously in two separate boxes. Three types of MC move are involved: (i) particle displacement for internal equilibrium, (ii) particle interchange for chemical equilibrium, and (iii) volume rearrangement for mechanical equilibrium. We used 500 particles in each simulation run. The simulation runs were conducted in cycles, with each cycle containing 500 particle displacements, 200–300 particle interchanges, and a single volume rearrangement. A complete simulation typically contained 10 000 cycles, the first 5000 used for equilibration and the final 5000 used to accumulate data. The final 5000 cycles were divided into ten blocks; the standard deviations were calculated from block averages.

The LJ part of the molecular interaction potential was truncated at half of each simulation box length, and the long-range correction to the LJ part was added by assuming the radial distribution function ($g(r)$) was equal to unity for distances greater than the cutoff distance. As the dipolar interaction is long range in nature, the standard cutoff approximation cannot be adopted for the conventional simulation size. Instead, special techniques such as the Ewald sum [18–20] or reaction field [19, 20] must be used to handle the long-range interactions. For the dipolar interaction part, an Ewald sum was used with the ‘tinfoil’ boundary condition [19]. Pretests demonstrated that a value of 5.0 for the parameter κ , which governs the convergence of the series in an Ewald sum, and 317 reciprocal lattice vectors gave good convergence results.

The chemical potentials were determined from the equation proposed by Smit and Frenkel [21]. It is obvious that for LJ particles the energy for a particle insertion into one phase, calculated during the particle interchange step, can also be used directly as the test particle energy for computing the chemical potential [10]. We note, however, that when

adopting the Ewald sum to handle the long-range dipole–dipole interactions the energy for inserting a real particle into the box contains the interaction energy of the inserted particle with all its *images*; this interaction energy should be excluded from the test particle energy.

All computations were carried out in reduced units. In table 1, we list all the reduced quantities used in this work.

Table 1. Definitions of reduced quantities.

Reduced dipole moment	μ^*	$\sqrt{\mu^2/\epsilon\sigma^3}$
Reduced pressure	P^*	$P\sigma^3/\epsilon$
Reduced temperature	T^*	$k_B T/\epsilon$
Reduced density	ρ^*	$(N/V)\sigma^3$
Reduced potential energy per molecule	E^*	$E/N\epsilon$
Reduced chemical potential	c^*	c/ϵ

P , pressure; N , number of molecules; T , temperature; k_B , Boltzmann constant; V , volume; E , total potential energy; c , chemical potential.

3. Results and discussion

3.1. Effects of dipolar interaction

Phase coexistence properties can be affected by any of the parameters in the potential models. The additional parameter in the SM potential model, the dipole moments of the particles, enables us to study the effects of dipolar interaction on the system's thermodynamic properties. To this end, we first set the LJ size and energy parameters, σ and ϵ , to be identical for both components and only varied the dipole moments in mixtures I–VI. The potential parameters for the binary mixtures and the corresponding temperature conditions are summarized in table 2 for mixtures I–VI; the simulation results are shown in table 3.

Table 2. Potential parameters and temperature conditions for the binary mixtures.

Mixture	T^*	σ_{11}^*	σ_{22}^*	ϵ_{11}^*	ϵ_{12}^*	ϵ_{22}^*	μ_1^{*2}	μ_2^{*2}
I	1.25	1.0	1.0	1.0	1.0	1.0	0.0	1.0
II	1.25	1.0	1.0	1.0	1.0	1.0	0.0	2.0
III	1.35	1.0	1.0	1.0	1.0	1.0	0.0	2.0
IV	1.35	1.0	1.0	1.0	1.0	1.0	0.0	3.0
V	1.35	1.0	1.0	1.0	1.0	1.0	1.0	2.0
VI	1.35	1.0	1.0	1.0	1.0	1.0	1.0	3.0
VII	0.9	1.0	1.0	1.0	0.7071	0.5	1.0	1.0
VIII	0.9	1.0	1.0	1.0	0.7071	0.5	1.0	0.0
IX	0.9	1.0	1.0	1.0	0.7071	0.5	0.0	1.0

Mixtures I and II are LJ–SM mixtures with the same reduced temperature, $T^* = 1.25$, but μ^{*2} is set at one and two, respectively. Figure 1 compares the vapour and liquid compositions, or phase envelope, for these two mixtures. It is clear that the composition of SM molecules is higher in the liquid phase than in the vapour phase, and that the higher the reduced dipole moment, the wider the phase envelope. This is again demonstrated in figure 2, which also compares two LJ–SM mixtures (mixtures III and IV), but at $T^* = 1.35$, and with higher reduced dipole moments of $\mu^{*2} = 2$ and $\mu^{*2} = 3$ for SM molecules in each fluid.

Table 3. GEMC simulation results for mixtures I–X. See table 2 for the intermolecular parameters. The values in parenthesis indicate the uncertainty in the last digit(s). P_{ext}^* is the imposed value of the pressure for the constant-pressure GEMC simulations; P_{int}^* is the pressure calculated in the simulation. x_1 is the relative composition of component 1.

P_{ext}^*	Vapour					Liquid						
	P_{int}^*	x_1	ρ^*	$-E^*$	$-C_1^*$	$-C_2^*$	P_{int}^*	x_1	ρ^*	$-E^*$	$-C_1^*$	$-C_2^*$
Mixture I												
0.063	0.0631(27)	0.055(5)	0.0700(50)	0.72(6)	7.50(9)	4.10(5)	0.054(24)	0.036(1)	0.6039(89)	4.74(7)	7.53(12)	4.06(25)
0.065	0.0650(22)	0.146(9)	0.0724(41)	0.72(4)	6.30(7)	4.21(5)	0.077(39)	0.100(6)	0.6003(237)	4.65(18)	6.20(14)	4.17(18)
0.070	0.0710(8)	0.183(8)	0.0842(23)	0.83(3)	5.92(6)	4.37(2)	0.081(28)	0.131(10)	0.6011(131)	4.63(10)	5.85(15)	4.17(22)
0.075	0.0754(29)	0.319(14)	0.0891(57)	0.82(5)	5.19(6)	4.19(2)	0.095(24)	0.246(13)	0.5912(196)	4.45(15)	5.15(13)	4.24(18)
0.080	0.0805(34)	0.438(12)	0.0993(76)	0.89(6)	4.75(6)	4.54(4)	0.073(15)	0.367(12)	0.5596(205)	4.11(15)	4.75(12)	4.51(17)
0.085	0.0843(22)	0.521(19)	0.1056(65)	0.93(7)	4.51(5)	4.69(6)	0.087(26)	0.480(19)	0.5495(217)	3.95(15)	4.44(14)	4.67(20)
0.090	0.0885(76)	0.608(20)	0.1155(246)	0.95(19)	4.29(9)	4.87(8)	0.095(13)	0.554(6)	0.5477(127)	3.90(9)	4.26(12)	4.74(13)
0.095	0.0919(31)	0.645(18)	0.1253(88)	1.05(6)	4.15(5)	4.97(4)	0.099(13)	0.591(5)	0.5590(138)	3.95(9)	4.10(6)	4.91(17)
0.097	0.0965(68)	0.739(11)	0.1417(324)	1.15(27)	3.98(5)	5.33(8)	0.097(17)	0.714(4)	0.5373(193)	3.74(13)	3.95(14)	5.29(11)
Mixture II												
0.028	0.0279(3)	0.172(9)	0.0264(5)	0.42(1)	6.96(6)	5.20(2)	0.032(24)	0.039(5)	0.7029(96)	6.83(9)	6.99(17)	4.92(66)
0.030	0.0301(8)	0.268(14)	0.0284(10)	1.41(2)	6.34(6)	5.27(5)	0.008(53)	0.066(18)	0.6965(119)	6.71(13)	6.27(16)	4.75(49)
0.035	0.0350(6)	0.361(22)	0.0334(9)	0.43(2)	5.81(7)	5.29(5)	0.017(48)	0.099(8)	0.6878(83)	6.52(10)	5.87(18)	5.13(28)
0.045	0.0453(10)	0.481(15)	0.0451(12)	0.51(1)	5.18(5)	5.28(3)	0.062(31)	0.158(13)	0.6850(89)	6.32(11)	5.19(19)	4.87(53)
0.055	0.0558(51)	0.621(17)	0.0583(82)	0.56(9)	4.65(11)	5.37(10)	0.040(36)	0.300(5)	0.6579(63)	5.73(6)	4.63(16)	5.19(36)
0.065	0.0694(66)	0.688(17)	0.0793(134)	0.08(1)	4.32(9)	5.49(10)	0.065(20)	0.416(20)	0.6361(95)	5.27(10)	4.29(13)	5.39(28)
0.075	0.0725(62)	0.711(20)	0.0831(110)	0.08(1)	4.24(8)	5.52(8)	0.067(19)	0.470(11)	0.6201(99)	5.01(9)	4.25(14)	5.41(33)
0.085	0.0838(25)	0.783(15)	0.1032(46)	0.10(1)	4.00(3)	5.77(7)	0.094(19)	0.616(10)	0.5921(131)	4.50(11)	4.01(13)	5.72(47)
0.090	0.0880(23)	0.784(13)	0.1145(88)	0.11(1)	3.97(3)	5.76(7)	0.105(26)	0.625(24)	0.5955(125)	4.50(12)	3.95(11)	5.61(39)
0.095	0.0944(28)	0.895(4)	0.1288(87)	0.13(1)	3.76(2)	6.51(5)	0.109(27)	0.862(5)	0.5339(235)	3.72(15)	3.80(9)	6.41(11)
Mixture III												
0.055	0.0552(20)	0.242(11)	0.0539(34)	0.73(5)	6.29(7)	5.03(5)	0.067(55)	0.077(8)	0.6455(106)	6.13(11)	6.30(18)	4.64(46)
0.060	0.0601(10)	0.302(14)	0.0588(19)	0.73(2)	5.90(7)	5.06(4)	0.070(33)	0.115(14)	0.6290(115)	5.88(13)	5.91(18)	4.88(31)
0.065	0.0648(23)	0.351(32)	0.0652(36)	0.77(6)	5.62(11)	5.12(8)	0.074(41)	0.140(16)	0.6256(148)	5.78(16)	5.59(15)	4.99(35)
0.070	0.0704(11)	0.427(18)	0.0711(19)	0.78(4)	5.29(6)	5.17(7)	0.062(42)	0.187(11)	0.6153(132)	5.59(11)	5.27(21)	5.08(47)
0.075	0.0749(21)	0.451(13)	0.0778(37)	0.84(5)	5.14(6)	5.16(5)	0.098(58)	0.226(25)	0.6073(217)	5.44(22)	5.07(16)	4.85(38)
0.085	0.086(38)	0.535(14)	0.0938(55)	0.93(6)	4.77(5)	5.26(4)	0.066(38)	0.309(22)	0.5822(195)	5.01(17)	4.75(10)	5.06(32)
0.100	0.1025(49)	0.582(21)	0.1296(124)	1.22(14)	4.48(5)	5.28(6)	0.111(26)	0.375(11)	0.5786(135)	4.85(11)	4.45(10)	5.07(37)
0.110	0.1100(51)	0.635(27)	0.1416(158)	1.25(16)	4.31(7)	5.36(6)	0.115(25)	0.464(20)	0.5413(219)	4.37(18)	4.32(10)	5.39(26)
0.120	0.110(14)	0.620(73)	0.255(160)	2.07(1.23)	4.25(4)	5.42(15)	0.113(20)	0.508(10)	0.5244(321)	4.17(23)	4.22(08)	5.46(38)

Table 3. (Continued)

P_{ext}^*	Vapour						Liquid					
	P_{int}^*	x_1	ρ^*	$-E^*$	$-c_1^*$	$-c_2^*$	P_{int}^*	x_1	ρ^*	$-E^*$	$-c_1^*$	$-c_2^*$
Mixture IV												
0.05	0.0506(9)	0.652(10)	0.0455(10)	0.52(2)	5.12(3)	6.27(6)	0.066(72)	0.107(9)	0.7270(107)	8.19(12)	5.12(19)	5.64(64)
0.06	0.0600(18)	0.707(21)	0.0552(21)	0.57(4)	4.82(5)	6.30(9)	0.071(33)	0.158(15)	0.7176(117)	7.86(19)	4.82(20)	5.66(77)
0.07	0.0696(26)	0.760(22)	0.0655(28)	0.62(3)	4.57(6)	6.40(8)	0.072(61)	0.209(12)	0.7000(114)	7.47(15)	4.54(21)	6.21(65)
0.08	0.0801(16)	0.792(11)	0.800(33)	0.73(5)	4.35(3)	6.44(6)	0.069(35)	0.273(34)	0.6816(156)	7.04(29)	4.36(18)	6.04(61)
0.09	0.0936(46)	0.819(15)	0.0988(63)	0.85(5)	4.16(4)	6.47(11)	0.082(35)	0.347(14)	0.6597(74)	6.52(10)	4.21(11)	6.8(1.5)
0.10	0.0971(54)	0.828(14)	0.1060(99)	0.90(9)	4.10(6)	6.51(8)	0.102(28)	0.396(15)	0.6483(86)	6.22(10)	4.12(9)	6.46(42)
0.11	0.1099(42)	0.819(24)	0.1328(132)	1.12(12)	3.99(4)	6.42(14)	0.112(20)	0.410(16)	0.6490(62)	6.17(8)	3.93(14)	6.08(53)
Mixture V												
0.050	0.0507(26)	0.166(8)	0.0501(35)	0.79(6)	7.01(4)	5.01(6)	0.048(20)	0.092(4)	0.6534(88)	6.28(9)	7.10(23)	4.91(43)
0.060	0.0603(20)	0.379(10)	0.0622(24)	0.85(4)	5.72(5)	5.22(4)	0.057(44)	0.251(10)	0.6390(96)	5.94(8)	5.63(21)	5.13(29)
0.070	0.0683(53)	0.505(13)	0.0748(91)	0.92(10)	5.19(8)	5.40(7)	0.074(19)	0.373(12)	0.6235(105)	5.64(9)	5.28(25)	5.34(34)
0.080	0.0768(43)	0.635(13)	0.0877(81)	1.00(10)	4.75(4)	5.68(6)	0.083(33)	0.507(4)	0.6101(89)	5.35(7)	4.71(8)	5.62(21)
0.095	0.0949(61)	0.860(6)	0.1171(149)	1.20(14)	4.19(4)	6.85(7)	0.092(10)	0.809(3)	0.5672(92)	4.64(6)	4.19(11)	7.00(19)
0.100	0.0997(78)	0.908(5)	0.1370(266)	1.34(24)	4.06(7)	7.28(12)	0.101(21)	0.874(4)	0.5541(161)	4.48(11)	4.06(10)	7.27(0)
Mixture VI												
0.04	0.0405(10)	0.645(13)	0.0370(12)	0.57(2)	5.45(5)	6.52(5)	0.055(58)	0.259(19)	0.7067(119)	7.67(17)	5.31(24)	5.75(74)
0.05	0.0503(14)	0.736(8)	0.0472(19)	0.64(3)	5.03(4)	6.70(4)	0.062(40)	0.401(20)	0.6765(89)	6.94(12)	4.91(27)	6.42(64)
0.06	0.0581(36)	0.8046(8)	0.0563(43)	0.68(5)	4.73(6)	6.89(7)	0.061(19)	0.514(7)	0.6576(78)	6.45(7)	4.78(32)	6.54(37)
0.07	0.0669(82)	0.820(19)	0.0686(112)	0.79(13)	4.57(11)	6.89(17)	0.066(29)	0.553(14)	0.6523(143)	6.28(13)	4.65(21)	6.88(64)
0.08	0.0799(75)	0.864(11)	0.0903(89)	0.95(10)	4.28(7)	7.01(15)	0.085(27)	0.688(8)	0.6291(75)	5.70(6)	4.25(16)	7.14(54)
0.09	0.0892(75)	0.921(7)	0.1111(258)	1.17(27)	4.14(9)	7.86(12)	0.093(30)	0.821(4)	0.5898(126)	5.04(10)	4.14(19)	7.77(18)

Table 3. (Continued)

P_{ext}^*	Vapour					Liquid						
	P_{int}^*	x_1	ρ^*	$-E^*$	$-c_1^*$	$-c_2^*$	P_{int}^*	x_1	ρ^*	$-E^*$	$-c_1^*$	$-c_2^*$
Mixture VII												
0.070	0.0691(26)	0.125(11)	0.1001(59)	0.50(4)	4.71(8)	2.57(3)	0.072(44)	0.779(19)	0.7501(86)	5.37(12)	4.59(62)	2.36(27)
0.080	0.0810(22)	0.121(23)	0.1233(52)	0.59(3)	4.73(15)	2.44(3)	0.091(27)	0.686(18)	0.7254(60)	4.86(9)	4.72(47)	2.31(23)
0.084	0.0831(32)	0.118(15)	0.1286(85)	0.61(5)	4.76(10)	2.43(3)	0.082(30)	0.669(11)	0.7158(51)	4.74(6)	4.72(26)	2.31(15)
0.090	0.0920(47)	0.114(12)	0.1516(141)	0.72(7)	4.78(9)	2.33(4)	0.095(21)	0.653(8)	0.7137(67)	4.68(6)	4.41(33)	2.30(16)
0.100	0.1038(60)	0.138(26)	0.1978(308)	0.94(16)	4.66(10)	2.27(5)	0.094(24)	0.640(17)	0.7099(107)	4.60(12)	4.61(43)	2.27(23)
0.110	0.1050(43)	0.135(26)	0.1993(346)	0.95(18)	4.71(11)	2.25(4)	0.111(33)	0.637(16)	0.7114(64)	4.60(8)	4.62(60)	2.30(12)
0.120	0.1192(99)	0.149(33)	0.2581(462)	1.20(25)	4.74(9)	2.17(4)	0.111(23)	0.584(16)	0.6892(75)	4.30(9)	4.70(24)	2.25(7)
0.130	0.123(18)	0.25(14)	0.393(169)	2.00(1.05)	4.68(12)	2.16(7)	0.128(27)	0.545(27)	0.6746(176)	4.08(18)	4.65(26)	2.16(15)
Mixture VIII												
0.08	0.0818(27)	0.123(15)	0.1160(49)	0.47(3)	4.60(9)	2.42(2)	0.079(38)	0.857(22)	0.7678(99)	5.70(16)	4.41(59)	2.33(16)
0.09	0.0898(30)	0.127(16)	0.1321(72)	0.54(3)	4.56(10)	2.34(3)	0.083(35)	0.878(23)	0.7774(108)	5.86(19)	4.13(46)	2.42(26)
0.10	0.0977(37)	0.115(18)	0.1476(69)	0.59(3)	4.63(11)	2.27(3)	0.085(24)	0.813(22)	0.7549(108)	5.40(17)	4.56(47)	2.23(28)
0.11	0.1097(47)	0.122(16)	0.1755(106)	0.70(5)	4.58(8)	2.19(3)	0.087(31)	0.823(11)	0.7595(80)	5.48(10)	4.62(43)	2.05(21)
0.12	0.1198(33)	0.120(21)	0.1957(69)	0.77(4)	4.62(14)	2.13(3)	0.136(43)	0.799(29)	0.7573(148)	5.37(22)	4.50(57)	2.01(26)
0.13	0.1328(55)	0.127(13)	0.2380(150)	0.94(5)	4.61(7)	2.04(2)	0.115(24)	0.717(32)	0.7251(167)	4.81(24)	4.62(78)	2.05(14)
0.14	0.1498(70)	0.147(9)	0.2989(258)	1.18(11)	4.59(4)	1.98(4)	0.143(29)	0.644(13)	0.6956(103)	4.34(11)	4.50(28)	2.00(11)
Mixture IX												
0.03	0.0300(6)	0.403(14)	0.0382(9)	0.23(1)	4.07(3)	3.58(3)	0.018(33)	0.922(11)	0.7324(64)	4.93(7)	4.12(41)	3.43(25)
0.04	0.0406(13)	0.362(17)	0.0543(21)	0.31(1)	3.96(4)	3.26(3)	0.051(38)	0.906(13)	0.7324(74)	4.87(8)	3.92(25)	3.17(28)
0.05	0.0501(6)	0.285(11)	0.0688(10)	0.36(1)	4.05(4)	2.99(2)	0.048(37)	0.864(27)	0.7217(151)	4.68(18)	3.95(30)	2.92(15)
0.06	0.0599(10)	0.264(6)	0.0870(23)	0.45(2)	4.03(2)	2.82(2)	0.070(41)	0.827(19)	0.7120(105)	4.50(12)	4.00(18)	2.75(14)
0.07	0.0701(23)	0.230(22)	0.1059(54)	0.52(3)	4.08(8)	2.66(4)	0.077(30)	0.783(19)	0.6992(95)	4.30(11)	4.15(26)	2.63(11)
0.08	0.0802(38)	0.218(20)	0.1296(85)	0.63(4)	4.09(7)	2.64(4)	0.086(16)	0.702(31)	0.6716(150)	3.93(16)	4.05(15)	2.57(9)
0.09	0.0902(49)	0.211(16)	0.1529(172)	0.73(9)	4.11(6)	2.46(4)	0.095(26)	0.655(12)	0.6572(90)	3.73(8)	4.20(12)	2.44(13)

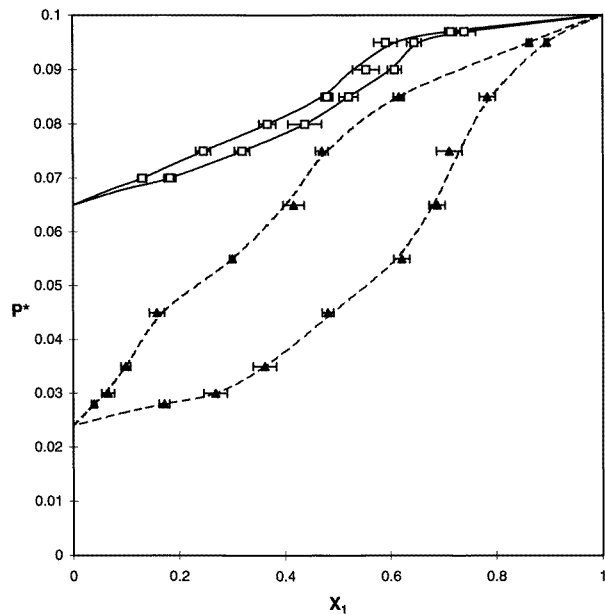


Figure 1. A comparison of the vapour-liquid phase envelope of mixture I (—□—) and mixture II (---▲---). X_1 is the relative composition of component 1. (See table 2 for the intermolecular parameters.)

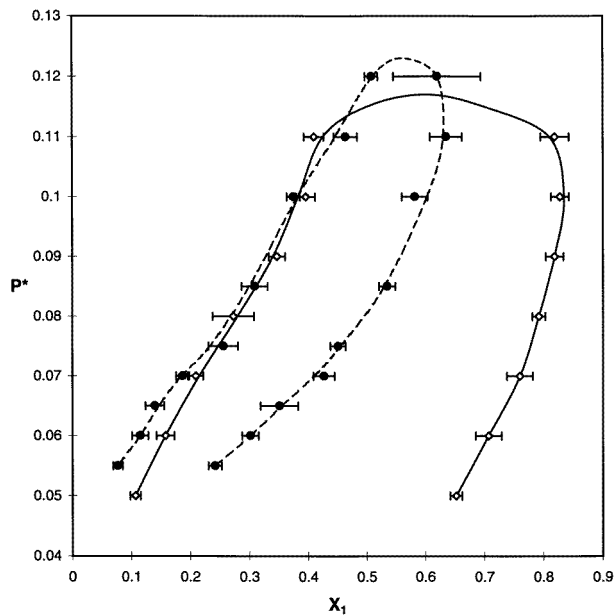


Figure 2. A comparison of the vapour-liquid phase envelope of mixture III (---●---) and mixture IV (—◇—). X_1 is the relative composition of component 1. (See table 2 for the intermolecular parameters.)

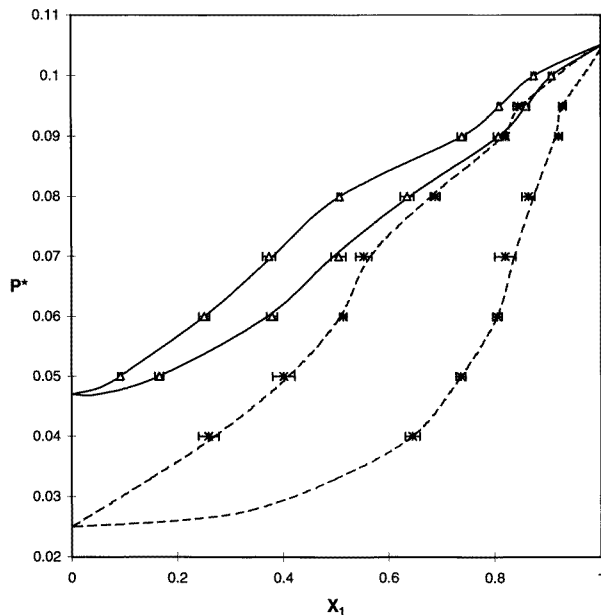


Figure 3. A comparison of the vapour–liquid phase envelope of mixture V (— Δ —) and mixture VI (---*---). X_1 is the relative composition of component 1. (See table 2 for the intermolecular parameters.)

Mixtures V and VI are SM–SM mixtures at $T^* = 1.35$. The reduced dipole moments of the molecules are one and two for mixture V, and one and three for mixture VI. The phase envelopes for these two mixtures appear in figure 3. Examination of these two envelopes suggests that a difference in the dipole moments of the two components affects the vapour and liquid compositions: the larger the difference, the wider the phase envelope.

Since, for all the mixtures discussed above, the differences in vapour and liquid compositions are solely brought about by the dipolar interaction, our simulation results show that the equilibrium compositions of both liquid and vapour phases are sensitive to the dipole moment difference between the two components: an increase in this difference causes the phase envelope to widen for both LJ–SM and SM–SM mixtures.

A salient feature of the phase diagrams for these mixtures is that the component which has a larger dipole moment tends to have a higher composition in the liquid phase than in the vapour phase. This indicates that the dipolar interaction is effectively attractive: the larger the molecular dipole moment, the stronger the attractive force, and thus the more difficult it is to separate the molecules, so molecules with a larger dipole moment are more likely to be in the liquid than gas phase. We also note that this attractive character of the dipolar interaction makes the critical temperature of the pure SM fluid higher than that of the pure LJ fluid [3].

3.2. Comparing the SM potential to the Keesom potential

In order to avoid dealing with the long-range nature of dipolar interactions, Sadus [15] used an angle-averaged dipolar interaction potential, called the Keesom potential, to represent the dipolar interactions in a study of VLE for systems containing dipolar components. His

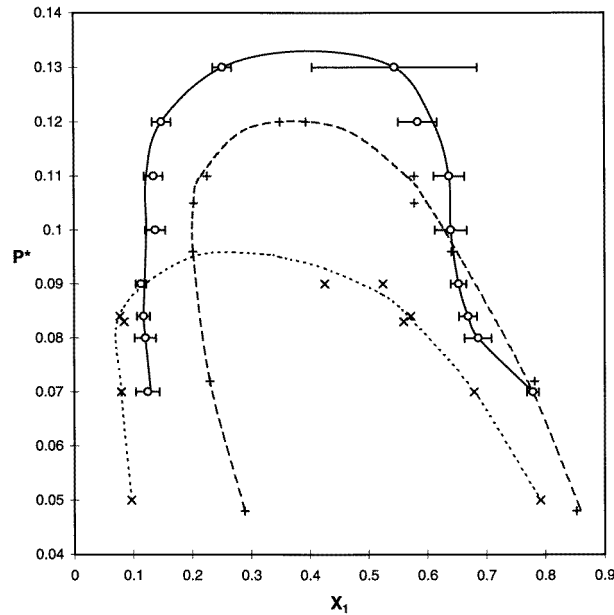


Figure 4. A comparison of the vapour-liquid phase envelope of mixture VII calculated with the SM potential (—○—), mixture VII calculated with the Keesom potential (- - - × - - -) by Sadus [15], and the LJ binary mixture (- - + - -) from Sadus [15]. X_1 is the relative composition of component 1. (See table 2 for the intermolecular parameters.)

GEMC results for one-component systems showed that the Keesom potential is an accurate alternative for the potential of the dipole-dipole interaction when $\mu^{*2} \leq 1$. In the same paper, he also presented the GEMC simulation results for binary mixtures at $T^* = 0.9$ and with the potential parameters listed in table 2 for mixtures VII-IX. However, he could not compare his results to the simulation results for the LJ-SM and SM-SM mixtures, as there had been no work reported for this problem at that time. For this reason, we have also conducted our simulations with the conditions in table 2 without angle-averaged approximations for the long-range dipolar interaction. Our simulation results for these mixtures are summarized in table 3.

In figure 4, we compare our results for mixture VII with the corresponding results obtained using the Keesom potential. Results for the LJ mixture at the same conditions are also shown. We see from this figure that adding the dipole moments of $\mu^{*2} = 1$ to the LJ molecules substantially lowers the vapour compositions for the component with the larger LJ energy parameter, but the liquid compositions do not show much difference for most of the phase envelope. This indicates that the attractive dipolar interaction affects the vapour composition more strongly than the liquid composition, and, for molecules with an identical dipole moment, the component with the larger LJ energy parameter tends to become more attractive to like molecules. However, the results of Sadus [15], obtained using the Keesom potential, show that both the vapour and liquid compositions of component 1 become lower, and its critical pressure is well below that of the LJ mixture. Conversely, our results show a slightly higher critical pressure than the LJ mixture.

Mixture VIII is the LJ-SM mixture in which the component with the larger LJ energy parameter has a dipole moment. In figure 5, it is clear that when the Keesom potential

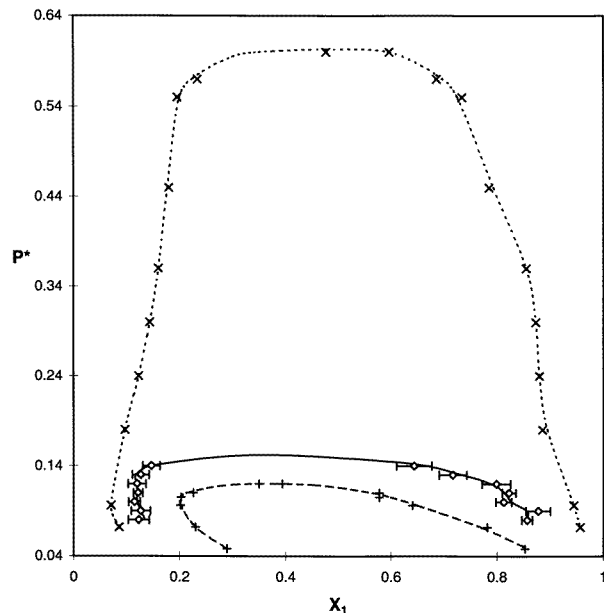


Figure 5. A comparison of the vapour–liquid phase envelope of mixture VIII calculated with the SM potential (—◇—), mixture VIII calculated with the Keesom potential (- - -x- - -) by Sadus [15], and the LJ binary mixture (- - + - -) from Sadus [15]. X_1 is the relative composition of component 1. (See table 2 for the intermolecular parameters.)

is used to represent the dipolar interaction there is a large deviation from the LJ mixture critical pressure. This is not the case when the realistic SM model is used, as only a small deviation from the LJ mixture is observed; the increase of the critical pressure is much smaller than that for the Keesom potential. Since the attractive force between the molecules of component 1 becomes even larger, the difference between the components becomes larger as well, and the phase envelope widens again.

Figure 6 compares VLE data on mixture IX, an LJ–SM mixture in which the component with the smaller LJ energy parameter has a dipole moment. The phase envelopes for our results, the results of Sadus using the Keesom potential to represent the dipolar interactions, and the LJ potential results of Sadus, are almost identical. This indicates that the dipolar interaction is not very strong in this case compared with the LJ interaction, and thus has little effect on the mixture's equilibrium properties. Only in this situation is the Keesom potential a good approximation of the dipolar interaction in mixtures.

From the above discussion, we see that adding the dipolar interaction to the LJ molecules with the larger energy parameter seems to have a more striking effect on the equilibrium compositions of the mixtures than adding the dipole moment to the molecules with the smaller energy parameter. The Keesom potential seems to overestimate the dipolar interaction in most cases when it is used to approximate the dipolar interaction.

4. Conclusion

Our results illustrate a trend in LJ–SM mixtures in which the phase envelope widens as the reduced dipole moment of the SM component increases. This trend also appears in SM–SM

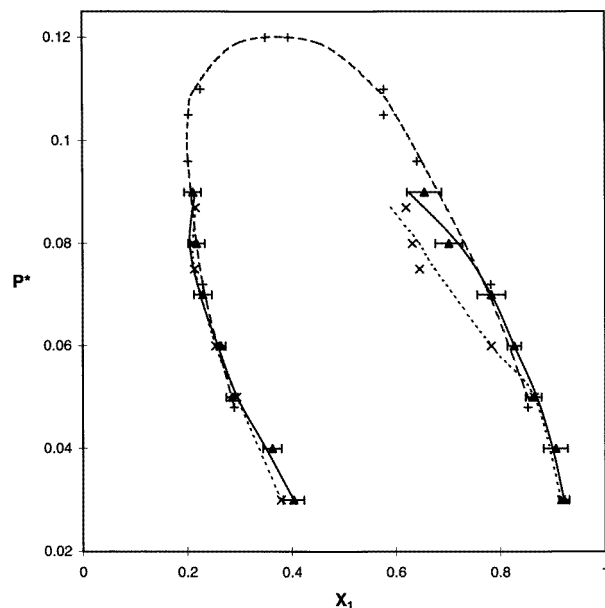


Figure 6. A comparison of the vapour–liquid phase envelope of mixture IX calculated with the SM potential (—▲—), mixture IX calculated with the Keesom potential (- - -×- - -) by Sadus [15], and the LJ binary mixture (- - -+ - -) from Sadus [15]. X_1 is the relative composition of component 1. (See table 2 for the intermolecular parameters.)

mixtures, where the phase envelope widens as the difference between the reduced dipole moments of the two components increases. Comparison of our results with those obtained using the Keesom potential emphasize the sensitivity of phase equilibrium properties to the molecular interaction potential used. Although for $\mu^{*2} \leq 1$ the Keesom potential can closely approximate the long-range dipole–dipole interaction for a one-component fluid, caution is required when dealing with mixtures containing dipolar components, as demonstrated in the present simulations. As the SM potential is very important for studying the effect of dipolar interaction on solutions, it has been our intention to quantify this effect in the LJ–SM and SM–SM mixtures and to provide reference data for future investigations.

Acknowledgments

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