

## RESEARCH NOTE

**Molecular simulation of the liquid-liquid equilibria of binary mixtures containing dipolar and non-polar components interacting via the Keesom potential**

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The Gibbs ensemble is used to simulate the liquid-liquid equilibria of binary mixtures containing dipolar and non-polar components. The interactions of the dipolar fluid are calculated using the Keesom intermolecular potential. The liquid-liquid coexistence properties are reported for different pressures and different combinations of dipolar/non-polar molecules. The critical properties of the mixtures are estimated. The ability of a dipole to induce phase separation is influenced by the dispersion energy of the molecule. Phase separation is enhanced if the dipolar molecule is also the component with the greatest dispersion energy.

**1. Introduction**

Liquid-liquid equilibria are commonly associated with mixtures containing dipolar molecules. Traditionally, the prediction [1] of the phase behaviour of dipolar molecules has relied on approximate methods such as perturbation theories [2, 3] or equations of state [4, 5]. Recently, improved algorithms [6, 7] have been reported that make possible the direct investigation of phase equilibria via molecular simulation. The application of molecular simulation methods to binary mixtures has focused mainly on vapour-liquid equilibria [6-10]. By contrast, simulations of liquid-liquid equilibria are relatively scarce and restricted largely to mixtures containing non-dipolar components [11-16]. No direct simulations of liquid-liquid equilibria involving a dipolar component have been reported. However, the effect of a dipole on liquid-liquid equilibria has been inferred from free energy of mixing calculations [17-19].

In contrast to the phase equilibria of non-polar fluids, the phase behaviour of dipolar fluids is complicated by the possibility of long range interactions. This is a problem for molecular simulation because intermolecular potentials that describe dipole interaction, such as the Stockmayer potential [20], cannot be truncated. Instead, special techniques such as the Ewald sum [21] or reaction field [21] must be used to account for long range interaction. Recently, we [22] used the angle-averaged Keesom potential [23, 24] to investigate vapour-liquid equilibria in both pure fluids and binary mixtures. In contrast to the Stockmayer potential, the Keesom potential is short ranged. Comparison with the results obtained [22] from the Keesom and Stockmayer potentials indicated that the Keesom potential was a reasonably accurate alternative for weak ( $\mu^{*2} \leq 1$ ) or moderately strong dipoles. It is conceivable that the Keesom potential may describe adequately the dipolar interactions of relatively simple molecules such as hydrogen chloride, trichloromethane and sulphur dioxide. The

Table 1. *NPT* Gibbs ensemble simulation of liquid–liquid coexistence at  $P^* = 0.125$  for binary mixtures with different combinations of dipolar and non-polar components.<sup>a</sup>

$T^*$	Liquid phase $\alpha$					Liquid phase $\beta$				
	$x_1$	$\rho^*$	$-E^*$	$-c_1^*$	$-c_2^*$	$x_1$	$\rho^*$	$-E^*$	$-c_1^*$	$-c_2^*$
$\mu_1^{*z} = 0; \mu_2^{*z} = 0$ (mixture I)										
0.94	0.286(48)	0.525(43)	2.33(19)	3.86	2.69	0.886(22)	0.726(11)	4.63(15)	3.86	2.69
0.915	0.201(43)	0.596(35)	2.59(14)	3.89	2.64	0.892(32)	0.740(9)	4.74(17)	3.89	2.64
0.905	0.157(26)	0.634(27)	2.74(11)	3.90	2.62	0.893(15)	0.741(6)	4.75(10)	3.92	2.60
0.9	0.146(21)	0.628(19)	2.71(8)	3.94	2.65	0.902(20)	0.743(8)	4.81(13)	3.93	2.69
0.85	0.082(22)	0.718(15)	3.13(7)	4.02	2.63	0.932(13)	0.777(7)	5.19(10)	4.08	2.64
0.8	0.041(8)	0.782(10)	3.45(5)	4.14	2.66	0.950(9)	0.800(4)	5.46(6)	4.06	2.70
$\mu_1^{*z} = 1; \mu_2^{*z} = 0$ (mixture II)										
1.17	0.387(12)	0.150(8)	0.75(4)	4.21	3.33	0.952(4)	0.718(5)	5.31(5)	4.25	3.21
1.15	0.324(21)	0.161(15)	0.78(7)	4.27	3.15	0.951(8)	0.730(14)	5.42(15)	4.31	3.12
1.12	0.288(14)	0.161(8)	0.77(4)	4.29	3.05	0.960(5)	0.754(10)	5.68(11)	4.31	3.06
1.1	0.254(29)	0.170(15)	0.81(7)	4.33	2.96	0.959(11)	0.761(16)	5.74(19)	4.36	2.94
1.05	0.170(19)	0.193(17)	0.91(8)	4.47	2.76	0.962(7)	0.780(8)	5.94(11)	4.57	2.77
1.0	0.090(10)	0.293(41)	1.35(17)	4.73	2.58	0.967(5)	0.809(6)	6.27(8)	4.73	2.62
0.95	0.039(9)	0.598(31)	2.60(13)	4.92	2.54	0.974(5)	0.831(5)	6.55(7)	4.88	2.50
0.9	0.025(10)	0.688(15)	3.00(6)	4.96	2.56	0.983(5)	0.861(5)	6.95(7)	4.86	2.42
$\mu_1^{*z} = 0; \mu_2^{*z} = 1$ (mixture III)										
1.02	0.331(66)	0.541(35)	2.60(16)	3.76	3.07	0.845(90)	0.664(34)	4.12(38)	3.78	3.08
1.01	0.177(34)	0.629(23)	2.99(11)	3.80	3.07	0.873(35)	0.678(19)	4.25(22)	3.80	3.07
0.99	0.111(41)	0.696(47)	3.36(24)	3.84	3.07	0.906(15)	0.702(9)	4.53(11)	3.81	3.08
0.98	0.084(27)	0.729(31)	3.54(17)	3.86	3.08	0.913(18)	0.708(7)	4.59(11)	3.85	3.11
0.97	0.065(11)	0.760(18)	3.72(10)	3.80	3.07	0.928(6)	0.721(7)	4.74(7)	3.82	3.08
0.95	0.049(9)	0.795(12)	3.93(7)	3.86	3.10	0.931(8)	0.727(4)	4.80(5)	3.89	3.11
$\mu_1^{*z} = 1; \mu_2^{*z} = 1$ (mixture IV)										
1.09	0.257(46)	0.424(91)	2.15(43)	4.47	3.08	0.872(45)	0.745(20)	5.25(34)	4.48	3.11
1.06	0.179(12)	0.604(45)	2.93(21)	4.52	3.05	0.904(12)	0.770(9)	5.58(13)	4.51	3.05
1.04	0.139(30)	0.656(26)	3.19(12)	4.60	3.07	0.918(16)	0.784(8)	5.79(13)	4.57	3.10
1.02	0.097(13)	0.712(7)	3.47(4)	4.64	3.02	0.915(21)	0.794(7)	5.88(15)	4.63	3.03
1.0	0.075(13)	0.747(20)	3.67(10)	4.67	3.01	0.922(8)	0.804(4)	6.00(6)	4.70	2.99
0.95	0.050(16)	0.798(16)	3.99(9)	4.86	3.16	0.950(14)	0.832(7)	6.44(13)	4.96	3.18

<sup>a</sup> The values in brackets indicate the uncertainty in the last digit.

Keesom potential has been fitted successfully [23] to the viscosity data for these molecules.

The aim of this work is to quantify the effect of dipole interactions by simulating the liquid–liquid equilibria of binary mixtures interacting via the Keesom intermolecular potential and comparing the results with calculations using the Lennard-Jones potential. Simulations are reported at various pressures for mixtures with different combinations of dipolar/non-polar components.

## 2. Theory

### 2.1. Intermolecular potential

The Keesom intermolecular potential [23, 24] combines the Lennard-Jones potential with a contribution from dipole interaction,

$$v(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] - \frac{\mu_i^2 \mu_j^2}{3kTr_{ij}^6}, \quad (1)$$

where  $\mu$  is the dipole moment,  $k$  is the Boltzmann constant,  $T$  is the temperature, and  $\varepsilon$  and  $\sigma$  are the characteristic depth and collision diameter, respectively, for the non-polar Lennard-Jones potential.

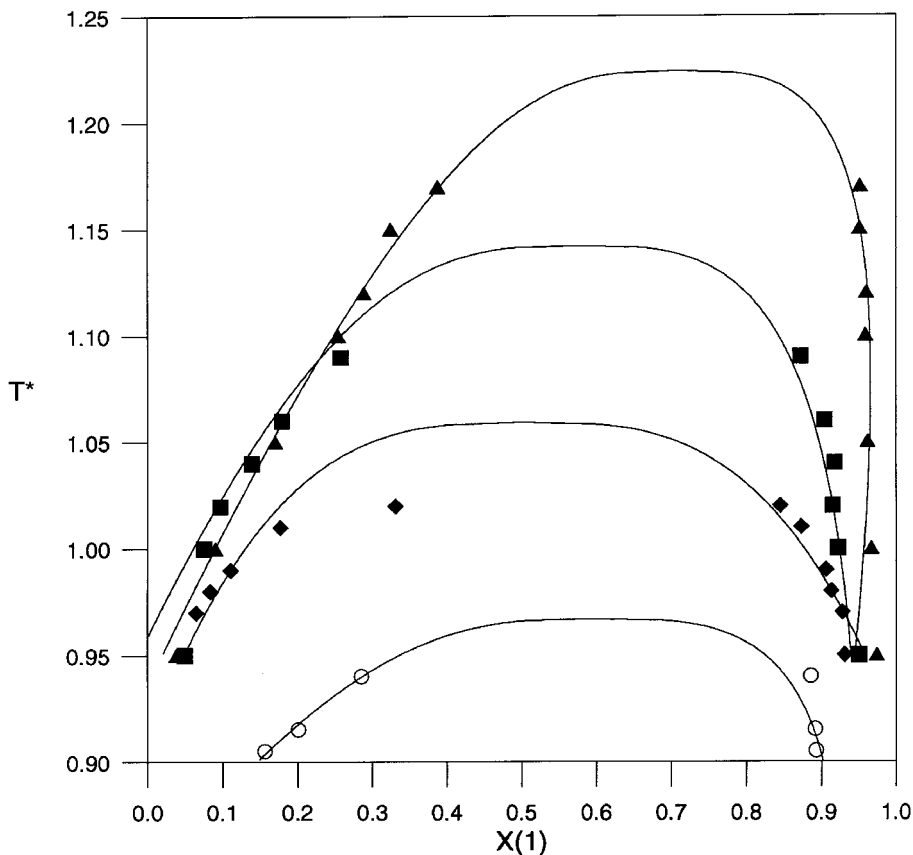


Figure 1. The effect of different combinations of dipolar/non-polar components on the liquid-liquid equilibria of binary mixtures at  $P^* = 0.125$ . Results are illustrated for mixtures I ( $\circ$ ), II ( $\blacktriangle$ ), III ( $\blacklozenge$ ) and IV ( $\blacksquare$ ).

It has been established [17–19] that, in the absence of weak unlike dispersion interactions, a large dipole moment is required to induce liquid-liquid equilibria in a binary mixture. Because equation (1) is valid [22] only for weak dipoles, we used values [15] of  $\epsilon$  and  $\sigma$  that are associated with liquid-liquid equilibria in a Lennard-Jones fluid. For all mixtures studied here:  $\epsilon_{22}/\epsilon_{11} = 0.75$ ,  $\sigma_{22}/\sigma_{11} = 0.95$ ,  $\epsilon_{12} = 0.7(\epsilon_{11}\epsilon_{22})^{1/2}$ , and  $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$ .

## 2.2. Simulation details

The *NPT* Gibbs ensemble method [7, 25] was used to simulate the liquid-liquid coexistence of different binary mixtures. We partitioned 300 molecules between two boxes to simulate the different liquid phases. The simulations were performed in cycles with each cycle typically consisting of 300 attempted displacements, a single volume fluctuation and 1000 interchange attempts. The maximum molecular displacement and volume changes were adjusted to obtain, when possible, a 50% acceptance rate for the attempted move. Ensemble averages were accumulated only after the system had reached equilibrium. The equilibration period was 7000–10 000 cycles and a further 7000–10 000 cycles were used to accumulate the averages. A typical run required approximately 1.5 CPU hours on a Fujitsu VP2200 computer, or approximately 7 CPU hours on a Cray YMP-EL computer.

Table 2. *NPT* Gibbs ensemble simulation of liquid–liquid coexistence of binary Lennard-Jones mixtures ( $\mu_1^{*2} = 0$ ;  $\mu_2^{*2} = 0$ ) at different pressures.<sup>a</sup>

$T^*$	Liquid phase $\alpha$					Liquid phase $\beta$				
	$x_1$	$\rho^*$	$-E^*$	$-c_1^*$	$-c_2^*$	$x_1$	$\rho^*$	$-E^*$	$-c_1^*$	$-c_2^*$
$P^* = 0\cdot25$ (mixture V)										
0·97	0·334(51)	0·619(10)	2·75(6)	3·66	2·47	0·835(70)	0·717(22)	4·38(30)	3·68	2·46
0·95	0·216(22)	0·644(15)	2·77(6)	3·67	2·45	0·868(19)	0·731(9)	4·56(13)	3·68	2·44
0·93	0·156(40)	0·677(15)	2·91(6)	3·73	2·42	0·872(20)	0·743(7)	4·66(2)	3·70	2·42
0·90	0·115(20)	0·708(17)	3·05(8)	3·75	2·43	0·898(26)	0·762(7)	4·91(15)	3·73	2·42
0·85	0·081(25)	0·757(19)	3·29(9)	3·78	2·47	0·942(15)	0·790(3)	5·32(8)	3·78	2·46
$P^* = 0\cdot5$ (mixture VI)										
0·99	0·219(75)	0·703(14)	3·02(5)	3·33	2·09	0·801(77)	0·739(13)	4·35(33)	3·32	2·07
0·98	0·152(26)	0·716(11)	3·04(5)	3·40	2·08	0·806(24)	0·739(6)	4·34(10)	3·39	2·09
0·95	0·139(30)	0·740(11)	3·16(5)	3·36	2·08	0·852(34)	0·759(6)	4·66(16)	3·38	2·06
0·90	0·073(19)	0·789(8)	3·40(4)	3·45	2·07	0·893(22)	0·784(10)	5·01(16)	3·55	2·06
0·85	0·055(20)	0·819(7)	3·56(4)	3·54	2·16	0·946(10)	0·814(5)	5·49(8)	3·40	2·16
$P^* = 1$ (mixture VII)										
1·06	0·249(51)	0·756(9)	3·20(3)	2·62	1·43	0·772(61)	0·761(8)	4·29(24)	2·64	1·42
1·04	0·179(32)	0·772(6)	3·24(3)	2·66	1·42	0·804(29)	0·771(5)	4·47(13)	2·65	1·42
1·02	0·142(16)	0·783(6)	3·28(3)	2·72	1·44	0·848(28)	0·783(4)	4·72(13)	2·65	1·45
0·99	0·115(25)	0·801(9)	3·38(4)	2·76	1·44	0·865(18)	0·791(2)	4·85(8)	2·73	1·45
0·975	0·104(17)	0·812(5)	3·43(2)	2·79	1·49	0·873(21)	0·799(5)	4·95(11)	2·81	1·50
0·95	0·085(16)	0·828(8)	3·52(4)	2·76	1·42	0·873(25)	0·805(4)	5·00(13)	2·87	1·37

<sup>a</sup> The values in brackets indicate the uncertainty in the last digit.

### 3. Results and discussion

The results of the *NPT* Gibbs ensemble simulations for the liquid–liquid coexistence of various binary mixtures are summarized in tables 1–3. The normal convention was adopted for the reduced density ( $\rho^* = \rho\sigma^3$ ), temperature ( $T^* = kT/\varepsilon$ ), energy ( $E^* = E/\varepsilon$ ), chemical potential ( $c^* = c/\varepsilon$ ), pressure ( $P^* = P\sigma^3/\varepsilon$ ), and dipole moment ( $\mu^{*2} = \mu^2/\varepsilon\sigma^3$ ). The chemical potential was determined from the equation proposed by Smit and Frenkel [26].

Guo *et al.* [15] reported that the values of  $\varepsilon$  and  $\sigma$  used in this work will result in liquid–liquid equilibria in a Lennard-Jones fluid at  $P^* = 0\cdot125$ . Our calculations at  $P^* = 0\cdot125$  (mixture I) confirm the existence of liquid phase separation in the Lennard-Jones fluid. The agreement with literature data [15] is within the combined uncertainties reported for the two simulations. Guo *et al.* [15] examined the effect of the  $\varepsilon_{12}$  and  $\sigma_{12}$  parameters on liquid–liquid coexistence. They concluded that liquid–liquid separation is enhanced by reducing the size of  $\varepsilon_{12}$  whereas the phase equilibrium is affected only marginally by changes in the  $\sigma_{12}$  parameter.

In addition to the Lennard-Jones system (mixture I), three distinct combinations of dipolar/non-polar molecules can be envisaged in a binary mixture. We can compose a mixture with a dipolar component 1 and a non-polar component 2 (mixture II) or vice versa (mixture III). Alternatively, both components can be dipolar (mixture IV). Our simulation results for these combinations of dipolar/non-polar components at  $P^* = 0\cdot125$  are summarized in table 1 and the coexistence curves are compared in figure 1. A reduced dipole moment of either 0 or 1 was used because previous work [22] indicated that the Keesom potential with these values represents accurately vapour–liquid equilibria.

It is apparent from figure 1 that the effect of a dipole is to increase the range of composition for which liquid–liquid separation occurs. The dipole also extends the

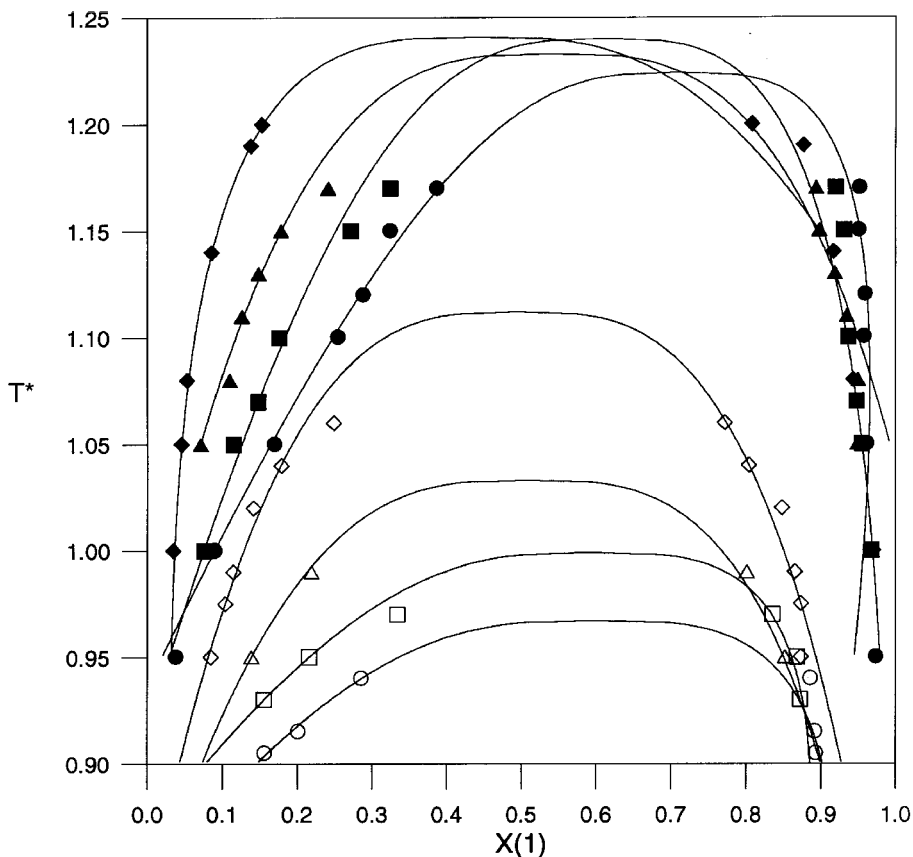


Figure 2. Comparison of the pressure dependence of liquid-liquid equilibria of Lennard-Jones mixtures (I, V-VII, open symbols) with mixtures containing a dipolar component (II, VIII-X, closed symbols):  $P^* = 0.125$  ( $\circ$ ,  $\bullet$ ),  $0.25$  ( $\square$ ,  $\blacksquare$ ),  $0.5$  ( $\triangle$ ,  $\blacktriangle$ ) and  $1$  ( $\diamond$ ,  $\blacklozenge$ ).

coexistence curve to substantially greater temperatures. The extent of phase separation depends on which component is dipolar. If component 2 is dipolar (mixture III), then a moderate increase is observed for the coexistence temperature when compared with the Lennard-Jones fluid (mixture I). A more significant increase in coexistence temperature is observed when both components are dipolar (mixture IV). However, the most significant effects are observed when component 1 is dipolar and component 2 is non-polar (mixture II). For mixture II, the dipolar component is also associated with the largest dispersion energy ( $\epsilon$ ). It appears that liquid-liquid phase separation is favoured when one component has both a dipole moment and greater dispersion energy than the other component. It has been reported previously [22] that the vapour-liquid equilibria of binary dipolar+non-polar mixtures interacting via the Keesom potential are affected substantially when the dipolar component is also the component with the largest dispersion energy.

It is of interest to compare the pressure dependence of the liquid-liquid equilibria of dipolar mixtures with the behaviour of Lennard-Jones mixtures. No data are available in the literature for the Lennard-Jones fluids at pressures other than  $P^* = 0.125$ . Consequently, simulations were performed first for Lennard-Jones mixtures at  $P^* = 0.25, 0.5$ , and  $1$  (table 2, mixtures V-VII). The temperature-composition

Table 3. *NPT* Gibbs ensemble simulation of liquid–liquid coexistence of binary dipolar + non-polar mixtures ( $\mu_1^{*2} = 1$ ;  $\mu_2^{*2} = 0$ ) at different pressures.<sup>a</sup>

<i>T</i> *	Liquid phase $\alpha$					Liquid phase $\beta$				
	$x_1$	$\rho^*$	$-E^*$	$-c_1^*$	$-c_2^*$	$x_1$	$\rho^*$	$-E^*$	$-c_1^*$	$-c_2^*$
<i>P</i> * = 0.25 (mixture VIII)										
1.17	0.324(31)	0.376(13)	1.71(7)	4.10	2.69	0.920(6)	0.721(7)	5.15(9)	4.10	2.70
1.15	0.271(31)	0.410(29)	1.80(12)	4.13	2.58	0.931(9)	0.743(14)	5.39(16)	4.16	2.60
1.1	0.176(34)	0.458(23)	1.97(10)	4.27	2.48	0.937(10)	0.761(8)	5.59(12)	4.38	2.52
1.07	0.148(36)	0.516(29)	2.20(12)	4.28	2.43	0.948(9)	0.780(8)	5.83(12)	4.27	2.43
1.05	0.115(25)	0.555(24)	2.37(10)	4.33	2.39	0.955(8)	0.790(7)	5.98(10)	4.28	2.44
1.0	0.076(21)	0.620(15)	2.65(6)	4.43	2.38	0.968(6)	0.819(3)	6.34(6)	4.50	2.38
<i>P</i> * = 0.5 (mixture IV)										
1.17	0.241(42)	0.589(13)	2.51(7)	3.78	2.08	0.894(32)	0.743(15)	5.15(24)	3.80	2.11
1.15	0.178(50)	0.600(14)	2.53(5)	3.89	2.07	0.898(29)	0.752(12)	5.25(23)	3.91	2.08
1.13	0.148(19)	0.618(10)	2.59(5)	3.91	2.04	0.919(9)	0.768(7)	5.49(10)	3.90	2.06
1.11	0.126(30)	0.640(14)	2.69(5)	3.90	2.00	0.935(9)	0.784(5)	5.72(8)	3.94	1.98
1.08	0.110(14)	0.657(14)	2.77(6)	3.92	2.03	0.950(10)	0.800(7)	5.96(11)	3.85	2.04
1.05	0.071(18)	0.685(14)	2.90(6)	4.12	2.01	0.949(12)	0.808(9)	6.05(14)	4.05	2.00
1.0	0.047(8)	0.722(8)	3.08(3)	4.18	2.01	0.964(12)	0.836(7)	6.43(13)	4.32	2.04
<i>P</i> * = 1 (mixture X)										
1.2	0.153(5)	0.705(5)	2.91(2)	3.21	1.31	0.808(50)	0.759(11)	4.79(29)	3.32	1.30
1.19	0.138(24)	0.711(10)	2.93(4)	3.20	1.32	0.877(40)	0.780(10)	5.27(25)	3.21	1.31
1.14	0.086(11)	0.740(9)	3.07(4)	3.33	1.31	0.917(8)	0.802(5)	5.68(8)	3.33	1.30
1.08	0.053(13)	0.777(8)	3.26(4)	3.51	1.31	0.944(11)	0.832(5)	6.12(10)	3.59	1.40
1.05	0.046(8)	0.791(6)	3.34(3)	3.47	1.33	0.959(9)	0.850(6)	6.41(10)	3.46	1.34
1.0	0.035(11)	0.816(9)	3.47(5)	3.57	1.39	0.970(7)	0.864(6)	6.65(9)	3.55	1.38

<sup>a</sup> The values in brackets indicate the uncertainty in the last digit.

projection of the coexistence curve for mixtures I and V–VII are compared in figure 2. It is apparent from Figure 2 that the effect of increasing pressure is to increase the range of composition at which two-phase liquid–liquid coexistence is observed. The temperature at which phase separation occurs also increases progressively with increasing pressure.

Table 3 summarizes the results of simulation at  $P^* = 0.25, 0.5,$  and 1 for dipolar + non-polar mixtures (VIII–X) with the dipole associated with component 1 (i.e.,  $\mu_1^{*2} = 1, \mu_2^{*2} = 0$ ). Figure 2 compares the liquid–liquid equilibria of the dipolar mixtures (II, VIII–X) with the non-polar mixtures (I, V–VII) at different pressures. It is evident from figure 2 that, irrespective of the pressure, the effect of the dipole of component 1 is to increase substantially both the composition range and temperature at which liquid–liquid phase separation occurs.

Gibbs ensemble simulations cannot be used to determine directly the critical point. However, the critical temperature  $T_c^*$  and critical composition  $x_c$  can be estimated by fitting the data to the following relationships:

$$x_\beta - x_\alpha = C \left| 1 - \frac{T^*}{T_c^*} \right|^{0.32}, \quad (2)$$

and

$$\frac{x_\beta^* + x_\alpha^*}{2} = A(T^* - T_c^*) + B. \quad (3)$$

The critical density can be obtained by using the density analogues of equations (2) and (3). The estimated critical properties are summarized in table 4.

Table 4. Estimated critical properties.<sup>a</sup>

Mixture	$\mu_1^{*2}$	$\mu_2^{*2}$	$P_c^*$	$T_c^*$	$\rho_c^*$	$x_c(1)$
I	0	0	0.125	0.967	0.552	0.599
II	1	0	0.125	1.224	0.322	0.709
III	0	1	0.125	1.059	0.616	0.503
IV	1	1	0.125	1.142	0.455	0.588
V	0	0	0.25	0.999	0.614	0.594
VI	0	0	0.5	1.033	0.675	0.508
VII	0	0	1.0	1.112	0.728	0.494
VIII	1	0	0.25	1.240	0.371	0.610
IX	1	0	0.5	1.233	0.605	0.539
X	1	0	1.0	1.241	0.708	0.441

<sup>a</sup> The uncertainties in the critical temperature, density and composition are  $\pm 0.01$ .

#### 4. Conclusion

The liquid–liquid phase coexistence of binary mixtures is influenced substantially by dipole interactions. The presence of a dipolar molecule increases both the coexistence temperature and the range of composition over which phase separation occurs. However, the ability of a dipole to induce phase separation also depends on the dispersion energy of the molecule. In a dipolar + non-polar mixture, phase separation is enhanced substantially if the dipolar molecule is also the component with the greatest dispersion energy. We [22] have reported a similar conclusion for the vapour–liquid equilibria of dipolar binary mixtures.

The simulations were performed on the Swinburne University of Technology Cray YMP-EL computer and the Australian National University Supercomputing Centre Fujitsu VP2200 computer.

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