Liquid-Liquid Equilibria for Polymer-Solvent Mixtures Using Improved van der Waals Equation of State

Ali Eliassi and Hamid Modarress

Chemical Engineering Faculty, Amir Kabir University of Technology, Tehran, I.R.Iran

ABSTRACT

In this work the improved van der Waals equation of state which has been used for vapour-liquid equilibria of polymer-solvent mixtures by previous workers, is extended to consider liquid-liquid equilibria by calculating and evaluating its third parameter (c) for several solvents and polymers such as benzene, cyclohexane, methylacetate, ethylacetate, propylacetate, acetone, polystyrene, polyisobutylene, polyvinylacetate. Also solvent activity in binary mixtures such as: benzene-polyisobutylene, cyclohexane-polyisobutylene, ethylacetate-polyvinylacetate, propylacetate-polystyrene, and acetone-poly-styrene at various concentrations is evaluated and compared with the experimental results and that of UNIFAC-FV results. The molar volume and activity calculation indicated that this equation has a higher predictability in phase equilibria calculation compared with methods such as UNIFAC-FV. The results showed that the improved van der Waals equation of state can give both upper and lower critical solution temperatures in liquid-liquid equilibria calculations, and this can be considered as an advantage over similar calculation procedures which can only give upper critical solution temperature. It has become evident, however, that using a suitable temperature functionality for the adjustable parameter, k_{ij}, can improve the results.

Key Words: thermodynamics, polymer solutions, liquid-liquid equilibria, phase equilibria, equation of state

INTRODUCTION

Solubility of polymers in solvents and the effect of temperature on it have been under considerable attention in polymer processing and applications. Therefore this field of research has attracted the interest of many research workers both in theoretical and experimental aspects. Due to the molecular differences between polymer and simple molecules, when they are used together in a mixture, several models have been proposed to study their thermodynamic behaviour. These thermodynamic models can be classified as follows [1]:
- noncompressible lattice models.
- compressible lattice models.
- off-lattice models.
- models based on generalized van der Waals partition function.

In the first group we can mention Flory-Huggins theory of polymer solutions [2, 3]. This theory, when it is used for *liquid-liquid equilibria* (LLE) calculation, can predict *upper critical solution temperature* (UCST) but faces limitation in predicting *lower critical solution temperature* (LCST).

Semiemperical methods, which are based on considering temperature and concentration functionality for χ in Flory-Huggins theory, have been proposed by Qian [4] and Bae [5]. This functionality enables the theory to predict both UCST and LCST as well as the effect of pressure [6] and molecular weight [7] on their variations.

On theoretical basis it is believed that free volume has a decessive effect on phase behaviour of the mixture [8] and noncompressible model does not include this effect.

In compressible model the free volume concept has been utilized to consider the phase behaviour of polymer mixtures. The assumptions are similar to that of Flory-Huggins [2, 3] and the free volume is assumed to be due to unoccupied sites in the lattice. In this respect the work of Costas [9], High and Danner [10−12], Panayioutou and Vera [13], and Sanchez and Lacomb [14, 15] are worth mentioning. Because the theory is complicated and several inherent parameters in the equation of state should be measured experimentally, they impose a limitation on applicability of this theory to any chosen mixtures.

In off-lattice model the continuity of polymer configurations is the essential assumption. Therefore, polymer chain is considered to consist of athermal hard spheres which are connected together [16−19].

Widespread attention has been paid to this model, but its efficiency remains to be proved yet.

In the fourth class of the models the *equation of state* (EOS) based on the van der Waals EOS can be mentioned. To develope this kind of EOS it is assumed that two parts constitute the molecular partition function, one for molecular interactions and the other for free volume effects [20, 21]. The theory of perturbed hard chain and related EOS are obtained also on this ground [1, 22−25].

The partition function for *improved van der Waals equation of state* (IVWEOS) has the following form:

$$Q = \frac{1}{N!}[\frac{V}{\Lambda^3}]^N [\frac{V_f}{V}]^N [\exp(-\frac{E_0}{2kT})]^N [Q_{r,v}]^N \qquad (1)$$

where N is the number of molecules in volume V at temperature T, Λ de Broglie wavelength, V_f free volume, k Boltzman constant, E_0 represents the potential field that each molecule experiences due to attractive forces of the other molecules, and N_A is Avogadro's number.

The free volume included in van der Waals partition function by Sako and Prausnitz [25] can be described as follows:

$$V_f = V - \frac{N}{N_A} b \qquad (2)$$

In eqn (1), the term $1/N! [V/\Lambda^3]^N$ is for translational contribution of ideal gas, $[V_f/V]^N [\exp(-E_0/2kT)]^N$ is for molecular interactions and $[Q_{r,v}]^N$ for vibrational degree of freedom. Following Prigogine, Beret and Prausnitz [26] factored $Q_{r,v}$ into an internal and an external parts, which the internal part depends only on temperature and the external part depends on density. Beret and Prausnitz assumed that the external rotational and vibrational degrees of freedom at liquid like densities can be considered as equivalent translational degrees of freedom. Beret and Prausnitz proposed a function for external part $(Q_{r,v}(ext))$ which is consistent with Prigogine's assumption at liquid densities and with the ideal gas law at low density:

$$Q_{r,v(ext)} = (\frac{V_f}{V})^{c-1} \qquad (3)$$

Where $3c$ is the total number of external degrees of freedom per molecule. For argon-like molecules, $c=1$ and for all other molecules $c=-1$. Parameter c reflects the looseness(or flexibility) of a molecule. Thus parameter c for a stiff rod is smaller than that for a soft (rubber-like) rod having the same dimensions.

Using partition function in eqn (1) the following EOS is obtained:

$$p = \frac{RT(\nu - b + bc)}{\nu(\nu - b)} - \frac{a}{\nu(\nu + b)} \qquad (4)$$

In eqn (4) ν is the molar volume, a, b and c are parameters of the equation. Where a is a function of temperature, b is independent of temperature variations, and $3c$ represents the total external degree of freedom of each molecule. When $c=1$, eqn (4) reduces to Redlich-Kwong EOS. The parameters a and b in eqn (4) can be obtained from following equations:

$$a(T=T_c) =$$

$$a_c = \frac{(1-2D_o+2cD_o+D_o^2-cD_o^2)(1+D_o)^2}{3(1-D_o)^2(2+D_o)} \times \frac{R^2T_c^2}{p_c} \qquad (5)$$

and:

$$b = \frac{D_o}{3} \times \frac{RT_c}{p_c} \qquad (6)$$

where T_c and p_c are critical temperature and pressure, respectively, and D_o is a function of parameter c:

$$D_o^3 + (6c-3)D_o^2 + 3D_o - 1 = 0 \qquad (7)$$

To consider the temperature functionality of a it is assumed that :

$$a = a_c \, \alpha(T) \qquad (8)$$

According to the results obtain by Sako et al. [25]:

$$\alpha(T) = \frac{\alpha_0(1-T_r^2)+2T_r^2}{1+T_r^2} \qquad (9)$$

where T_r is the reduced temperature and α_o is obtained from following equation:

$$\alpha_0 = 1.1920 + 0.11060 \ln(V_w) + 0.30734 \times 10^{-3} V_w \qquad (10)$$

V_w is the van der Waals volume which can be calculated from Bondi's group contribution [27].

The eqn (9) cannot be used for polymers, because the critical properties do not exist for

them. Therefore, we have to find another method for calculating parameter a in eqn (4). Parameter a depends on the interaction of molecules and London formula for dispersion forces [28], and it is appropriate for calculating parameter a if the following assumptions are valid:

- the polymer molecules can be divided in equal segments.

- potential energy between two adjacent nonbonded segments can be given by random dispersion formula.

- the potential energy of the entire system is pairwise additive.

Then [25]:

$$a = 0.1659 \left(\frac{A^2I}{V_w^2}\right)_{sat.m} V_{w(polymer)} \, r.\exp(-2.3731 \, \tilde{T}) \qquad (11)$$

where A is molar polarization of segment, I is the first ionization potential, V_w is van der Waals volume, and r is number of segments which can be calculated by the ratio of molar volume of each species to the species which is considered as $\tilde{T}$ solvent in the mixture. $\tilde{T}$ can be expressed as:

$$\tilde{T} = \frac{ckT}{\varepsilon} \qquad (12)$$

and:

$$\varepsilon = \left(\frac{9}{16\pi^2}\right) \frac{r}{N_A} \left(\frac{A^2I}{V_w^2}\right)_{sat.m} \qquad (13)$$

where k is Boltzman constant and sat.m was used to represent hydrogenated monomer.

Sako et al. have shown that for parameter b the following equation is appropriate:

$$b = 1.3768 \, V_w \qquad (14)$$

where V_w for polymers can be obtained by Bondi's method for monomer and then multiplying by degree of polymerization.

Sako et al. [25] used the IVWEOS to study liquid-vapour equilibria for the system of ethylene-polyethylene at high pressure. They have also calculated the parameter c for a number of normal alkanes. But no attempt has been made so far to

extend the application of this equation to study LLE for polymer-solvent systems. Therefore, considering the relative simplicity and applicability of this equation for obtaining the required data for chemical processing it was decided to use this equation to study LLE for polymer-solvent systems. The polymer-solvent systems selected for this work are those which are widely used in polymer industries.

CALCULATIONS

Calculation of Parameter c for Solvents

To examine the accuracy of equation of state, eqn (4), it was used to calculate molar volume of solvents. To do this parameter c was calculated from density data [29], and V_w by Bondi's method [27]. Then from eqns (5–10) the parameters a and b were calculated. Inserting values of a, b and c in eqn(4) the molar volume at 1 atm and different temperatures was calculated. The results for c, V_w are reported in Table 1. Molar volumes at different temperatures are reported in Table 2. The relative percent error shown in this table for different solvents, substantiate the accuracy of EOS and validity of the values of c obtained.

Calculation of Parameter c for Polymer

The purpose of this work is to consider LLE calculations for polymer solutions at the pressure of 1 atmosphere and the temperatures 270–550 K. The parameters a and b in the equation of state, eqn (4), can readily be calculated by eqns (11) and (14).

Table 1. Parameter c and van der Waals volume for some solvents.

Solvent	c	V_w (cm³/mol)
Benzene	1.706	48.36
Cyclohexane	1.436	56.80
Methylacetate	2.448	42.54
Ethylacetate	1.589	52.77
Propylacetate	2.561	63.00
Acetone	3.067	39.04

Table 2. Calculated molar volume (cm³/mol) for some solvents.

Solvent	T(K)	V_{cal}	Relative percent error
Benzene			
	273	86.33	−0.38
	298	89.02	−0.32
	320	91.73	−0.07
	330	93.08	+0.11
	340	94.52	+0.33
	353	96.55	+0.71
Cyclohexane			
	278	105.99	+0.009
	298	108.56	+0.06
	310	110.25	+0.14
	330	113.36	+0.35
	400	128.52	+2.78
Methylacetate			
	273	76.06	−1.40
	300	79.78	−0.32
	320	83.01	+0.74
	330	84.82	+1.37
Ethylacetate			
	273	105.75	−0.80
	300	109.86	−0.43
	330	115.38	+0.40
	350	119.81	+1.30
Propylacetate			
	273	112.29	−1.93
	298	115.81	−1.36
	320	119.16	−0.66
	340	122.44	+0.18
	360	125.95	+1.29
	374.6	128.68	+2.32
Acetone			
	273	70.79	−0.84
	300	74.48	+0.45
	320	77.69	+1.73
	329.5	77.49	0.0

Only parameter c needs some extra calculations which are based on density calculation and are described as follows:

Tait equation [30], which is obtained on

Table 3. Parameter c for polymers at 270–500 K.

Polymer	c
PS	272.07
PIB	152.60
PVAC	274.12

fitting of experimental data for specific volume of polymers at a given temperature and pressure, is presented as:

$$V(p,T) = V(0,T)[1 - 0.0894 \ln(1 - \frac{p}{B(T)})] \quad (15)$$

where:

$V(p,T)$: specific volume in m^3/kg at pressure p and temperature T.

$V(0,T)$: specific volume in m^3/kg at zero pressure and temperature T.

$B(T)$: Tait parameter for the polymer in Pascal.

p: pressure in Pascal.

T: temperature, Kelvin.

The specific volume at zero pressure is given by:

$$V(0,T) = A_0 + A_1(T - 273.15) + A_2(T - 273.15)^2 \quad (16)$$

where:

A_0, A_1, A_2: specific constants for the polymer [30].

The Tait parameter, $B(T)$ is a function only of temperature and is given by:

$$B(T) = B_0 \exp[-B_1(T - 273.15)] \quad (17)$$

B_0, B_1: specific constants for the polymer [30].

The value of density obtained from eqn (15), for a given polymer, was introduced in eqn (4) and the best value for c was calculated. The results are reported in Table 3.

Calculation of Activity of Solvent by EOS
For phase equilibria calculations the condition for equilibrium requires the equality of activities for species, therefore, the activities of solvent and polymer should be known. The activity of species i is defined as:

$$a_i = \frac{\tilde{\phi_i}}{\phi_i^*} \quad (18)$$

where $\tilde{\phi_i}$ and ϕ_i^* are fugacity coefficients of i in the mixture and in pure state at 1 atm pressure, respectively. The fugacity coefficient of pure i, ϕ_i^* can be calculated from the following equation:

$$\ln \phi_i^* = -\ln\frac{p(v - b)}{RT} - \frac{a}{bRT} \ln(1 + \frac{b}{v}) + (\frac{pv}{RT} - 1) - \ln(\frac{v - b}{v})^{c-1} \quad (19)$$

The fugacity coefficient of i in mixture $\tilde{\phi_i}$ can be calculated by the following equation:

$$\ln\tilde{\phi_i} = \frac{1}{RT} \int[(\frac{\partial p}{\partial n_i})_{T,v,n_j} - \frac{RT}{v}]dv - \ln Z =$$

$$-\ln\frac{p(v - b_m)}{RT} - \frac{1}{RT}[\frac{2\sum_j x_j a_{ij}}{b_m} - \frac{a_m b_i}{b_m^2}]\ln[1 + \frac{b_m}{v}] -$$

$$\frac{a_m b_i}{b_m RT(v + b_m)} + \frac{b_i c_m}{(v - b_m)} - \ln(\frac{v - b_m}{v})^{c_i - 1} \quad (20)$$

where a_m, b_m and c_m are obtained using the following well known mixing rule:

$$a_m = \sum_i \sum_j x_i x_j a_{ij} (1 - k_{ij}) \quad (21)$$

$$b_m = \sum_i x_i b_i \quad (22)$$

$$c_m = \sum_i x_i c_i \quad (23)$$

where x is mole fraction, a_{ii}, b_i and c_i represent the parameters for pure species and k_{ij} is an adjustable parameter.

In this work we are dealing with two component systems of polymer solvent. The activity of solvent was calculated by eqns (18–23) and the activity of polymer will be discussed later.

Calculation of Activity of Solvent by UNIFAC-FV
We use UNIFAC-FV [31] to obtain activity of solvent and compare results of calculation for activity of solvent by EOS, as described in previous section.

In UNIFAC-FV the activity of component i,

Table 4. Activity of benzene (a_1) in (benzene-PIB) mixture.

ϕ_2	$a_1^{exp.}$ [32]	a_1^{IVW}	(E%)$_{IVW}$	a_1^{UF} [31]	(E%)$_{UF}$
0.600	0.954	0.966	1.26	0.977	+2.41
0.692	0.923	0.905	1.92	0.942	+2.06
0.738	0.862	0.859	−0.36	0.885	+2.67
0.815	0.761	0.745	−2.14	0.877	+15.24
0.892	0.537	0.558	+3.87	0.517	−3.72

$\overline{M}_v$=40,000; T=298 K; k_{ij}=−0.9928; ϕ_2 = volume fraction of polymer; $a_1^{exp.}$ = activity of solvent (experimental); a_1^{IVW} = activity of solvent (improved van der Waals EOS); a_1^{UF} = activity of solvent (UNIFAC-FV); (E%)$_{IVW}$ = relative percent error (van der Waals EOS); (E%)$_{UF}$ = relative percent error (UNIFAC-FV).

Table 5. Activity of cyclohexane in (cyclohexane-PIB) mixture.

ϕ_2	$a_1^{exp.}$ [33]	a_1^{IVW}	(E%)$_{IVW}$	a_1^{UF} [31]	(E%)$_{UF}$
0.390	0.960	0.950	−1.04	0.932	−2.92
0.559	0.876	0.867	−1.05	0.837	−4.45
0.660	0.784	0.782	−0.22	0.746	−4.85
0.784	0.610	0.621	+1.75	0.575	−5.74
0.852	0.463	0.491	+5.96	0.444	−4.10

$\overline{M}_v$=40,000; T=298 K; k_{ij}=−0.0588.

Table 6. Activity of ethylacetate in (ethylacetate-PVAC) mixture.

ϕ_2	$a_1^{exp.}$ [31]	a_1^{IVW}	(E%)$_{IVW}$	a_1^{UF} [31]	(E%)$_{UF}$
0.474	0.925	0.916	−0.96	0.898	−2.92
0.548	0.870	0.873	0.32	0.833	−4.25
0.665	0.767	0.772	0.60	0.717	−6.52
0.738	0.683	0.681	−0.26	0.615	−9.96
0.800	0.580	0.582	0.36	0.517	−10.86
0.846	0.483	0.491	0.02	0.417	−13.66

$\overline{M}_v$=110,000; T=303 K; k_{ij}=−0.1763

a_i are expressed as:

$$\ln a_i = \ln a_i^c + \ln a_i^r + \ln a_i^{fv} \qquad (24)$$

where a_i^c, a_i^r and a_i^{fv} are combinatorial, residual and free volume activity, respectively. The results are tabulated in Tables 4–8, and they are compared with experimental results. Also, in the tables the values of k_{ij} are reported for the systems.

Calculation of Polymer Activity

The activity of polymer cannot be calculated directly neither by EOS nor by UNIFAC-FV. Therefore, Gibbs Duhem equation can be used to calculate activity of polymer:

$$\Sigma \, x_i \, d\overline{M}_i = 0 \qquad (25)$$

Using eqn (25) for polymer solvent mixture the

Table 7. Activity of propylacetate in (propylacetate-PS) mixture.

ϕ_2	$a_1^{exp.}$ [34]	a_1^{IVW}	$(E\%)_{IVW}$	a_1^{UF} [31]	$(E\%)_{UF}$
0.445	0.990	0.994	0.40	0.996	0.61
0.545	0.950	0.959	0.93	0.963	1.37
0.622	0.906	0.910	0.39	0.914	0.88
0.667	0.880	0.869	−1.26	0.872	−0.91
0.756	0.763	0.756	−0.90	0.753	−1.31
0.831	0.618	0.619	−0.10	0.600	−2.91

$\bar{M}_n = 290,000$; T=298 K; $k_{ij} = -0.8144$.

Table 8. Activity of acetone in (acetone-PVAC) mixture.

ϕ_2	$a_1^{exp.}$ [31]	a_1^{VDW}	$(E\%)_{IVW}$	a_1^{UF} [31]	$(E\%)_{UF}$
0.418	0.934	0.962	3.02	0.907	−2.89
0.610	0.817	0.828	1.40	0.780	−4.53
0.740	0.685	0.678	−1.05	0.641	−6.42
0.870	0.509	0.465	8.59	0.417	−18.07

$\bar{M}_v = 110,000$; T=303 K; $k_{ij} = -0.4966$.

following equation is obtained:

$$a_p = \exp\left[-\frac{M_p}{M_s} \int_0^{a_s} \frac{x_s}{x_p} \times \frac{da_s}{a_s}\right] \qquad (26)$$

where a_p and a_s are each the activity of polymer and solvent, respectively, and x_p and x_s are the mole fractions.

To obtain a_p, the activity of solvent a_s is calculated by EOS and then it is substituted in eqn (26). The Gauss Legendre [36] method is used to calculate the integral.

Liquid-Liquid Phase Equilibria Calculation

For polymer-solvent mixture at the temperature well below the boiling point there may exist two phases namely polymer dissolved in solvent (L1), making a true solution, and solvent dissolved in polymer, making a gel solution (L2). As the temperature is increased these two phases will dissolve in each other and the system will show a temperature known as UCST. As the temperature is decreased, again the system will change from two phase to one phase and then the system will show an LCST.

In our calculation we have obtained the activity of solvent from the EOS by eqns (17−22). The activity of polymer is then calculated by eqn (26). The equilibrium point at a temperature for a given composition is where the activity of solvent is equal for the phases present in the system. The results are depicted in Figures 1−5.

RESULTS AND DISCUSSION

Comparing the molar volume of solvent at 273 K up to the normal boiling point (Table 2) indicates

Table 9. Relative percent error of IVWEOS and UNIFAC-FV for some polymer-solvent systems.

System	$(E\%)_{IVW}$	$(E\%)_{UF}$
Benzene−PIB	0.81	5.22
Ethylacetate−PVAC	0.42	8.03
Cyclohexane−PIB	2.00	4.41
Propylacetate−PS	0.60	1.33
Acetone−PVAC	3.52	7.98
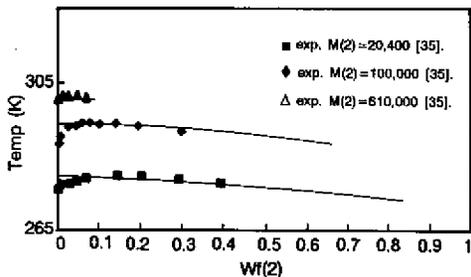
Solid lines are calculated with $k_{ij} = 0.1097-7.9\times10^{-6}\ T_r$, $k_{ij} = 1.4358-9.4\times10^{-6}\ T_r$ and $k_{ij} = 1.6192-1.1\times10^{-5}\ T_r$ for molecular weights 20.4×10^3, 100×10^3, 610×10^3, respectively.
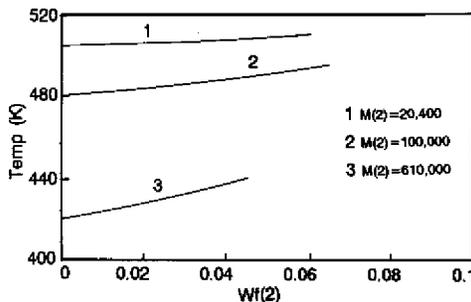
Figure 1. Phase diagrams of cyclohexane (1)/PS (2) UCST.

that, IVWEOS, using the parameters obtained for it, has high quality for calculating the molar volume.

Also, comparing the activity of solvent obtained by IVWEOS with those obtained by UNIFAC-FV (Tables 4−8) indicates that the former gives the percent error of 1.47, while for UNIFAC-FV the error is 5.3 (Table 9).

Figures 1−5 show the phase diagrams of some polymer-solvent mixtures. The increasing trend of UCST with molecular weight of polymer is consistent with experimental data.

In cyclohexane/polystyrene mixtures where

Solid lines are calculated with $k_{ij} = 0.1097-7.9\times10^{-6}\ T_r$, $k_{ij} = 1.4358-9.4\times10^{-6}\ T_r$ and $k_{ij} = 1.6192-1.1\times10^{-5}\ T_r$ for molecular weights 20.4×10^3, 100×10^3, 610×10^3, respectively.

Figure 2. Phase diagrams of cyclohexane (1)/PS (2) LCST.
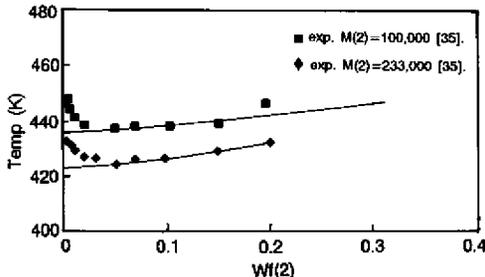
Solid lines are calculated with $k_{ij} = -1.3+5.52\times10^{-6}\ T_r$ and $k_{ij} = -2.1 + 7.85\times10^{-6}\ T_r$ for molecular weights 100×10^3, 233×10^3, respectively.

Figure 3. Phase diagrams of ethylacetate (1)/PS (2) LCST.

the molecular weights of polystyrene are 20,400, 100,000, and 610,000, the IVWEOS gives UCST which agrees with experimental results. For these systems LCST has not been reported but IVWEOS can give a reasonable results as it is seen in Figure 2.

Following the ideas used by Orbey [37], Schwartzentruber [38] and Bonner [39] about the temperature functionality of k_{ij}; in this work this functionality is presented in following form:
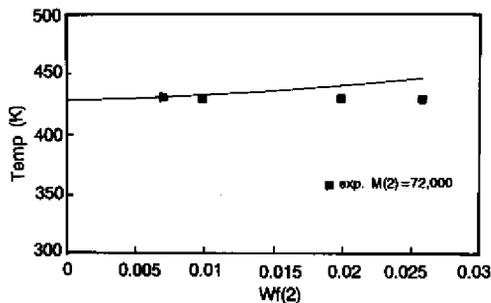
$$k_{ij} = a + bT_r \qquad (27)$$

where T_r is reduced temperature of solvent, a and b are adjustable parameters.

This functionality not only improves the results but also gives both UCST and LCST.
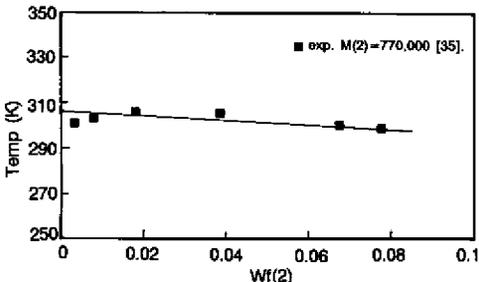
Solid line is calculated with $k_{ij} = -2.305 + 7.03\times10^{-7}\ T_r$.

Figure 4. Phase diagrams of methylacetate (1)/PS (2) LCST.

Solid line is calculated with $k_{ij} = -0.987 + 3.58 \times 10^{-6} \, T_r$.

Figure 5. Phase diagrams of n-hexane (1)/PIB (2) LCST.

CONCLUSION

The IVWEOS was used to calculate parameter c for several different solvents and polymers. The solvent activity was calculated for solutions having different concentrations of polymer. It was shown that if the parameter of this equation is exactly known, it can give solvent activity with excellent precision.

Also using a suitable functionality of temperature for interaction parameter (k_{ij}) IVWEOS can give the UCST and LCST with good accuracy.

The LLE calculations for several polymer-solvents were calculated and were reported. The dependency of LLE diagrams on polymer characteristics such as molecular weight is also depicted in this work.

NOMENCLATURE

A: molar polarization (cm³/mol)
A_0: specific constant in eqn (16)
A_1: specific constant in eqn (16)
A_2: specific constant in eqn (16)
B(T): Tait parameter
B_0: specific constant in eqn (17)
B_1: specific constant in eqn (17)
D_o: constant determined from parameter c
E_o: potential field (cm³ bar/molecule)
I: first ionization potential per mole (cm³ bar/molecule)

M_i: molecular weight
$\bar{M}_i$: partial molar property of component i
N: number of molecules
N_A: avogadro's number
p: pressure in equation (15) (pascal)
p_c: critical pressure
Q: canoncial partition function
$Q_{r,v}$: partition function for rotations and vibrational degrees of freedom
$Q_{r,v(ext)}$: external part of $Q_{r,v}$
R: gas constant (cm³bar/mol K)
$\tilde{T}$: defined in eqn (12)
T: temperature (K)
T_r: reduced temperature
T_c: critical temperature (K)
$V_{(p,T)}$: specific volume at pressure p and temperature T (m³/kg)
$V_{(0,T)}$: specific volume at zero pressure and temperature T (m³/kg)
V_w: van der Waals volume (cm³/mol)
V_f: free volume (cm³)
V: volume (cm³)
Z: compressibility factor in eqn (19)
a: energy parameter in EOS (cm⁶ bar/mol²)
$\grave{a}$: adjustable parameter in eqn (38)
a_i: activity of component i
a_c: defined in eqn (5)
a_m: parameter a in mixture
a_{ii}: parameter a for pure species
a_i^c, a_i^r, a_i^{fv}: combinatorial, residual and free volume activity
a_p: activity of polymer
a_s: activity of solvent
b: volume parameter in EOS (cm³/mol)
$\grave{b}$: adjustable paramtere in eqn (27)
b_m: parameter b in mixture
b_i: parameter b for pure species
3c: total number of external degree of freedom for molecule
c_i: parameter c for pure species
c_m: parameter c in mixture
k: Boltzman constant (cm³ bar/molecule k)
k_{ij}: binary interaction parameter
p: pressure (bar)
r: number of segments per molecule

w_i: weight fraction of component i
x_i: mole fraction of component i

GREEK SYMBOLS

Λ: de Broglie wavelength (cm)
$\alpha(T)$: defined in eqn (9)
α_o: defined in eqn (10)
ε: characteristic energy (cm³ bar/molecule)
ν: molar volume (cm³/mol)
ϕ_i^*:   fugacity coefficient of i in pure state
ϕ_i: fugacity coefficient of i in pure mixture

ACKNOWLEDGEMENT

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