



PREDICTING LIQUID–LIQUID TRANSITIONS IN POLYMER SOLUTIONS USING THE GCLF EQUATION OF STATE

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Abstract—Group contribution lattice fluid equation of state (GCLF-EOS) have been extended and used to calculate phase equilibria in polymer solutions. Group parameters for three group contributions and nine new group contributions have been calculated. Saturation vapor pressure for pure solvent and weight fraction activity coefficients in polymer solutions have been calculated and the agreement obtained with experimental data indicated the accuracy of the parameters. A combining rule consisting a pair interaction parameter with temperature dependency was proposed. The area method was used with GCLF-EOS to obtain phase diagram for liquid equilibrium (LLE) of polymer solutions. The method was able to predict both lower critical solution temperature (LCST) and upper critical solution temperature (UCST). © 1998 Elsevier Science Ltd. All rights reserved

Key words—Equation of state, Polymer solution, Liquid–liquid equilibria, Group contribution

NOMENCLATURE

<i>a</i>	Activity, adjustable parameter defined by equation (13)
<i>b</i>	Adjustable parameter defined by equation (13)
<i>e</i>	Functional group parameter
<i>G</i>	Gibbs free energy (J K ⁻¹)
<i>k</i>	Boltzman constant, adjustable parameter defined by equation (12)
<i>M_w</i>	Molecular weight (g g mol ⁻¹)
<i>n</i>	Number of group
<i>N</i>	Number molecules
<i>P</i>	Total pressure
<i>q</i>	Effective chain length of molecule (dimensionless)
<i>Q</i>	UNIFAC surface area (dimensionless)
<i>r</i>	Number of segment of a molecule (dimensionless)
<i>R</i>	Universal gas constant
<i>R</i>	Group reference volume (m ³ kmol ⁻¹)
<i>T</i>	Absolute temperature
<i>V</i>	Molar volume
<i>w</i>	Weight fraction
<i>x</i>	Mole fraction
<i>z</i>	Lattice coordination number (dimensionless)
<i>Γ</i>	Non-randomness factor of component
<i>ε</i>	Interaction energy
<i>η</i>	Molecular surface fraction of component (dimensionless)
<i>θ</i>	Overall surface fraction (dimensionless)
<i>λ</i>	Non-random auxiliary parameter
<i>μ_i</i>	Chemical potential of component <i>i</i>
<i>φ_i</i>	Segment fraction of component <i>i</i>

Subscripts

H	Hole
<i>i</i>	Component <i>i</i>
<i>i</i> – <i>j</i>	Quantity pertaining to contact of type <i>i</i> – <i>j</i>
<i>i</i> ,p	Quantity pertaining to pure component <i>i</i>

<i>k</i>	Group
<i>m</i>	Group
<i>s</i>	Solvent
sp	Specific

Superscripts

*	Reducing quantities
~	Reduced quantities
I&II	Phase

INTRODUCTION

Application of equations of state for predicting thermodynamic properties of molecular fluids in pure and mixed states has been quite successful. However for macromolecular fluids, such as polymers and their solutions, due to complications inherent in their chain configurations, it is a new subject for research. Recently the wide spread use of polymers and the need for their synthesis has increased the interest and thereby research on the field of polymer solutions. Improved thermodynamic behavior prediction of polymer solutions may lead to a better understanding of many processes which involve polymer synthesis and separation of polymer impurities. Phase equilibria play an important role in the processing and application of polymers. Knowledge about the equilibrium behavior of specific polymer systems is often necessary in order to design polymer manufacturing processes or to predict process performance.

Undoubtedly, polymer activity models, such as the Flory–Huggins theory [1] and its many modifications, have been quite popular for correlation and prediction of phase equilibrium of polymer sol-

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Table 1. Group contributions for the GCLF-EOS. In this table e , R and Q functional group parameters in equations (14)–(16) at 300 and 400 K

Groups	Ref.	e_{300}	e_{400}	R_{300}	R_{400}	Q
CH ₃	[10]	640.870	640.790	0.01596	0.01628	0.848
CH ₂	[10]	943.330	987.680	0.01524	0.01498	0.540
CH	[10]	2209.380	2708.760	0.01311	0.01175	0.228
C	[10]	5378.380	7731.240	0.01071	0.08463	0.150
CY–CH ₂	[10]	895.440	911.400	0.01260	0.01256	0.540
CY–CH	[10]	1727.560	2043.280	0.01255	0.01199	0.228
CY–C	[10]	4069.490	5993.670	0.01242	0.01126	0.150
Ac–H	[10]	975.380	971.620	0.01059	0.01073	0.400
Ac–CH ₃	[10]	994.410	1022.680	0.02465	0.02456	0.968
Ac–CH ₂	[10]	1471.590	1581.800	0.02351	0.02302	0.660
Ac–CH	[10]	2780.930	3281.530	0.02220	0.02060	0.348
Ac–C	[10]	5452.730	6771.480	0.01985	0.01700	0.270
–O–	[10]	868.470	679.560	0.00760	0.00798	0.240
H ₂ O	[10]	949.120	1154.310	0.07611	0.07544	1.400
CH ₃ C=O ^d	[10]	1237.100	1171.500	0.03117	0.03254	1.488
–CH ₂ C=O–	[10]	1542.0	1509.500	0.02968	0.03039	1.180
–CHCl–	[10]	1364.400	1387.300	0.04865	0.05036	0.952
Ac–Cl	[13]	1214.350	1236.200	0.02242	0.02255	0.844
–CH ₂ –NH ₂	[13]	1199.240	1085.460	0.02206	0.02315	1.236
–CH ₂ (NH)–	[13]	1208.900	1197.500	0.02486	0.02467	0.936
Ac–OH	[13]	2572.600	2358.000	0.01273	0.01296	0.680
CHCl ₃	[13]	994.670	930.670	0.05376	0.06095	2.410
–(CH ₃)C(CH ₃)–	[13]	854.430	927.660	0.04320	0.04155	1.696
CH=CH–	[14]	1054.480	1110.630	0.02412	0.02390	0.867
–COO ^a	[14]	1341.670	1308.800	0.02236	0.02327	1.200
–OH–	[14]	1867.920	1466.870	0.00685	0.00752	1.200
–CH ₂ NH–	[14]	1280.830	1215.760	0.02490	0.02443	0.936
>SiO<	[14]	1064.430	1343.840	0.03376	0.03285	0.4657
Ac–CO–	[14]	2181.980	2275.410	0.02105	0.02263	0.760
COOH	present work	2534.500	2033.700	0.01259	0.01961	1.224
HCOO–	present work	1440.334	1163.300	0.01259	0.02870	1.188
CH ₂ –Cl	present work	1224.015	1001.076	0.01981	0.03549	1.264
CH ₂ =CH–	present work	739.663	585.100	0.02856	0.04181	1.176
Ac–NH ₂	present work	2307.830	2129.000	0.01435	0.01498	0.816
Ac–F	present work	812.310	612.580	0.01600	0.03200	0.524
CH ₃ –SH	present work	959.770	859.770	0.03473	0.04310	1.676
–CH ₂ –SH	present work	1502.680	1274.300	0.01386	0.02413	1.368
CCl ₄	present work	918.188	855.688	0.07307	0.08973	2.910
–O ^b	present work	2167.400	806.500	0.01100	0.02782	0.240
–COO ^b	present work	1236.665	1074.000	0.02713	0.04711	1.200
CH ₃ C=O ^c	present work	1548.886	1329.600	0.01781	0.02669	1.488

^aFor polymers.^bFor solvents.^cFor ketone group in acetone.^dFor all ketone groups except in acetone.

utions. Recently, the field of polymer solution thermodynamics has been proliferated with the activity coefficient and equation of state models based on the group contribution methods [2–5]. Among the assumptions necessary to relate the activity coefficients to group contributions, are the hypothetical group-activity-coefficients, which are defined for functional groups in molecules, and the mixing

rules which are adopted to relate group contributions to the molecular parameters of activity coefficients. Although the activity coefficient models provide convenient ways to estimate the phase equilibrium behavior of polymer solutions from a limited data, they suffer from the inherent empiricism in their derivations from of the original Flory–Huggins theory.

Table 2. Comparison of percentage average errors for calculated vapor pressure with the improved and old group parameters

Component	T rang (K)	Present	Old
Methyl ether	233–323	14.16	299.85
Ethyl ether	243–403	35.58	92.40
Methyl ethyl ether	273–373	11.65	148.44
Methyl propyl ether	283–313	65.18	147.16
Ethyl propyl ether	273–433	37.90	62.91
Methyl acetate	273–433	93.84	104.48
Ethyl acetate	263–463	46.90	48.26
Propyl acetate	273–483	18.12	19.14
Methyl propionate	263–463	52.18	55.66
Methyl butyrate	273–483	20.51	24.73
Isopropylisobutyrate	283–473	49.43	172.32
Acetone	283–463	6.34	38.13

Table 3. Comparison of percentage average errors for predicted weight fraction activity coefficient with the improved and old group parameters

System	Polymer M_w	T (K)	w_s rang	Improved	Old
PVC/di- <i>n</i> -propyl ether	34,000	315.35	0.0378–0.2156	11.923	31.897
PS/ <i>n</i> -butyl acetate	500,000	293.15	0.0810–0.308	18.143	23.428
PS/ <i>n</i> -propyl acetate	290,000	298.15	0.0690–0.553	7.027	12.167
	290,000	343.15	0.0630–0.679	3.222	9.150
PPOX/benzene	1,500,000	320.35	0.1305–0.6868	2.195	1.709
	1,500,000	333.35	0.2101–0.6848	3.668	1.036
	1,500,000	343.05	0.0910–0.4856	6.391	1.036
	1,500,000	347.85	0.0884–0.6791	5.927	1.509
PVA/benzene	48,200	303.15	0.0620–0.555	11.877	7.625

Prediction of vapor liquid equilibria is based on $k_{ij}=0$.

PS = Polystyrene, PVC = Polyvinylchloride, PPOX = Polypropylene oxide, PVA = Polyvinylacetate.

Experimental data as in Ref. [14].

In this study, we present application of a molecular thermodynamics framework of the group contribution lattice fluid, GCLF, equation of state for predicting phase equilibrium in binary mixtures of polymer–solvent systems. It is shown that not only the vapor–liquid equilibrium, but also the liquid–liquid equilibrium (LLE) and lower and upper critical solution temperatures (LCST and UCST) can be predicted quite accurately with the proposed framework.

APPLICATION OF THE GCLF-EOS TO POLYMER SOLUTIONS

The expressions for the pressure, P , and activity, a , of component i based on the group-contribution lattice fluid equation of state (GCLF) [5] used in the present work are as follows:

$$\tilde{P} = \tilde{T} \ln(\tilde{V}/(\tilde{V} - 1)) + 0.5z\tilde{T} \ln[(\tilde{V} + q/r - 1)/\tilde{V}] - \theta^2 \quad (1)$$

$$RT \ln a_i = \ln \varphi_i + \ln(\tilde{V}_i/\tilde{V})$$

$$+ q_i \ln[\tilde{V}(\tilde{V}_i - 1)/\tilde{V}_i(\tilde{V} - 1)] + q_i[(2\theta_{i,p} - \theta)/\tilde{T} - \theta/\tilde{T}] \quad (2)$$

In the above expressions $\tilde{P}=P/P^*$ is the reduced pressure, $\tilde{V}=V/V^*$ is the reduced volume, and $\tilde{T}=T/T^*$ is the reduced temperature, z is the lattice coordination number, r is the number of segments, q is the effective chain length of molecule (dimensionless), θ is the surface fraction, $\theta_{i,p}$ is the surface fraction of component i , and P^* , T^* , V^* are the reducing pressure, temperature, and volume, respectively. Parameters r , q , θ , V^* , and φ_i are defined by the following expressions:

$$r = \sum x_i r_i \quad (3)$$

$$q = \sum x_i q_i \quad (4)$$

$$\theta = qN/(N_H + \sum q_i N_i) \quad (5)$$

$$V^* = \sum x_i V_i^* \quad (6)$$

$$\varphi_i = r_i x_i / r \quad (7)$$

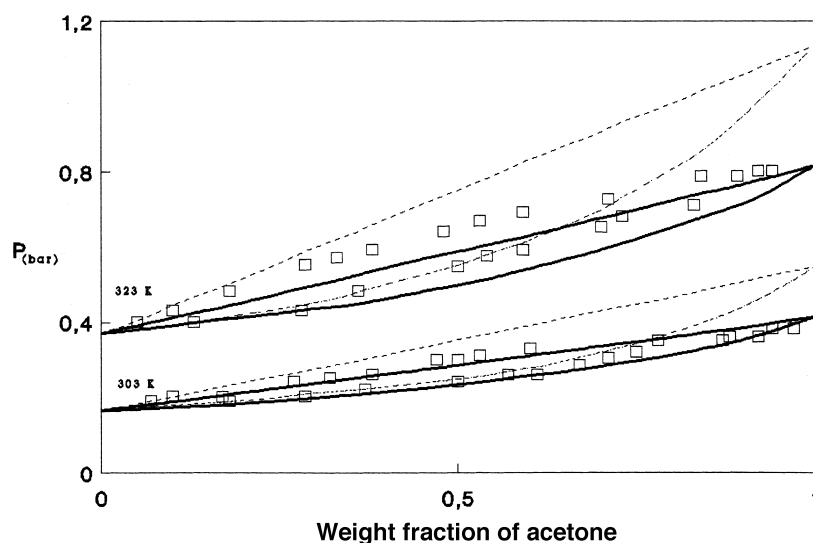


Fig. 1. Comparison of experimental and calculated data with improved group parameters and old group parameters of $\text{CH}_3\text{-CO-}$ for vapor liquid equilibria of acetone/benzene system at two temperatures [15]. Calculation curves are based on $k_{ij}=0$. (--- old, — improved, □ expt. data.)

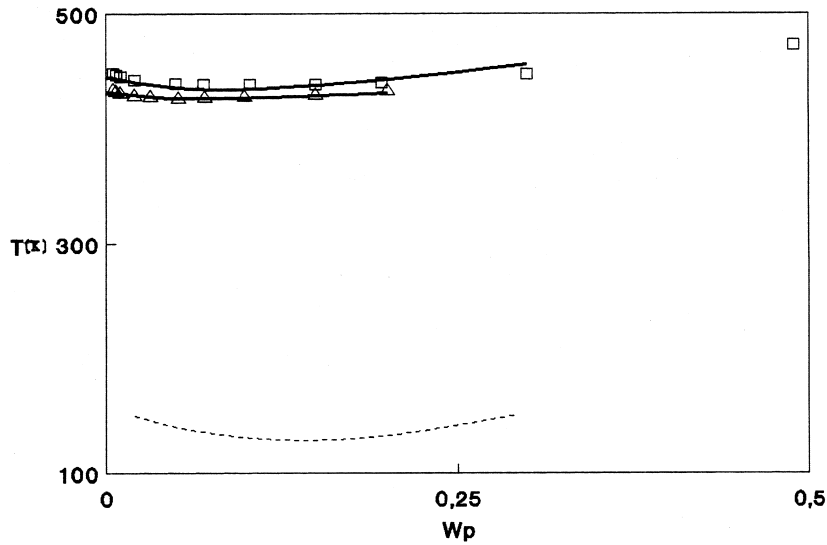


Fig. 2. Cloud point temperature (LCSTs) as a function of polymer weight fraction for polystyrene/ethylacetate system at 2 molecular weights of polymer. --- is calculation curve with $k_{ij}=0$ for $M_w=100000$ for polystyrene. (— calculation with k_{ij} , \square $M_w=100,000$, \triangle $M_w=233,000$, --- $M_w=100,000$, $k_{ij}=0$.)

where N is the number of molecules and N_H is the number of vacant site or holes. Also the following expression is defined for z :

$$ze^*/2 = P^*V_H = kT^* \quad (8)$$

where the lattice site volume, $V_H=9.75 \times 10^{-3} \text{ m}^3/\text{kmol}$, $z = 10$, and the characteristic energy, ϵ^* , for a binary mixture is given by [6]:

$$\epsilon^* = \epsilon_{11}\eta_1 + \epsilon_{22}\eta_2 - \eta_1\eta_2\Gamma_{12}^0(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}) \quad (9)$$

where $\eta_i = q_i x_i / q$, and Γ_{12}^0 is a factor for non-random contacts between segments of component 1 and 2:

$$\Gamma_{12}^0 = 2/(1 + [1 - 4\eta_1\eta_2(1 - \lambda_{12})]^2) \quad (10)$$

and

$$\lambda_{12} = \exp[\theta(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})/(kT)] \quad (11)$$

ϵ_{ij} are for the $i-j$ pair potential and if i is not equal j they are obtained from the combining rules such as [7]

$$\epsilon_{ij} = \sqrt{(\epsilon_{ii} \times \epsilon_{jj})}(1 - k_{ij}) \quad (12)$$

where k_{ij} is the unlike-interaction parameter which is an adjustable.

In polymer solutions the temperature-dependency of k_{ij} appearing in equation (12) is in a form which needs to be considered [8,9]. It is suggested that this adjustable parameter should be chosen as a function of temperature. Of course, such functional-

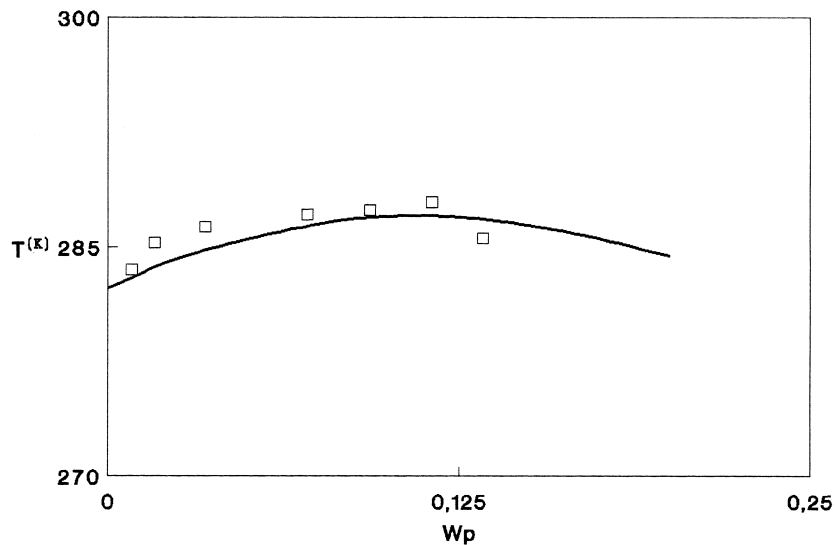


Fig. 3. Cloud point temperature (UCST) as a function of polymer weight fraction for polystyrene/methylacetate ($M_w=179300$). (— calculation, \square expt. data.)

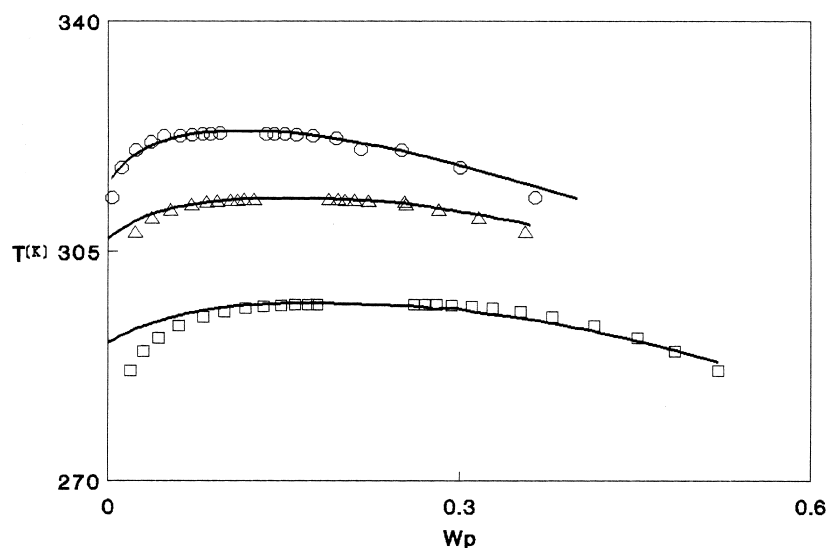


Fig. 4. Effect of molecular weight of polystyrene/methylcyclohexane on UCST curve. (— calculation, \square $M_w = 17,200$, \triangle $M_w = 46,400$, \circ $M_w = 109,000$.)

ity often is used for low molecular weight mixtures. In this work we propose the following linear temperature functionality for this adjustable parameter:

$$k_{ij}(T) = a_{ij} + b_{ij} \cdot T \quad (13)$$

where a_{ij} and b_{ij} are assumed to be constant characteristic of the components i, j .

Groups of molecules have been used for calculating molecular parameters of GCLF-EOS. The molecular parameters V_i^* and ε_{ii} are calculated by the following group contribution expressions [5, 10]:

$$V_{i,T}^* = a_T + \sum n_k R_{k,T} \quad (14)$$

$$\varepsilon_{ii,T} = \sum \sum \Theta_k \Theta_m \sqrt{e_{kk,T} \cdot e_{mm,T}} \quad (15)$$

$$\Theta_k = \frac{n_k Q_k}{\sum n_m Q_m} \quad (16)$$

where e_{kk} , R_k and Q_k are functional group parameters.

The interaction energy ε_{ii} and the reducing molar volume V_i^* are calculated at two temperatures of 300 K and 400 K from the group contributions given in Table 1. These values are used to linearly interpolate for the temperature of interest. The value of a_T at 300 K, (a_{300}), is 0.02123 and (a_{400}) is

Table 4. Coefficients of $k_{ij} = a_{ij} + b_{ij}T$ for various polymer–solvent systems

Polymer	Polymer M_w	Solvent	Kind of phase diagram	a_{ij} [-]	b_{ij} [(1/K) $\times 10^3$]
Polystyrene	100,000	ethylacetate	LCST	-1.02025	1.665
Polystyrene	233,000	ethylacetate	LCST	-3.16372	6.901
Polystyrene	179,300	methylacetate	UCST	-0.14392	-0.600
Polystyrene	17,200	methylcyclohexane	UCST	0.12083	-0.400
Polystyrene	46,400	methylcyclohexane	UCST	0.15163	-0.480
Polystyrene	109,000	methylcyclohexane	UCST	0.13359	-0.420
Polystyrene	43,600	cyclohexane	UCST	0.11177	-0.370
Polystyrene	80,000	cyclohexane	UCST	0.11432	-0.370
Polystyrene	89,000	cyclohexane	UCST	0.10372	-0.340
Polystyrene	97,000	cyclohexane	UCST	0.22811	-0.770
Polystyrene	97,130	cyclohexane	UCST	0.15633	-0.530
Polystyrene	250,000	cyclohexane	UCST	0.15412	-0.500
Polystyrene	1,270,000	cyclohexane	UCST	0.14424	-0.470
Polystyrene	100,000	tert-butylacetate	LCST	0.01216	-0.120
Polystyrene	100,000	tert-butylacetate	UCST	0.19946	-0.770
Polystyrene	233,000	tert-butylacetate	LCST	-0.11388	0.163
Polystyrene	233,000	tert-butylacetate	UCST	0.13297	-0.490
Polystyrene	10,300	acetone	LCST	-0.13406	-0.360
Polystyrene	10,300	acetone	UCST	0.20701	-0.670
Polystyrene	20,400	acetone	LCST	-0.00903	0.0483
Polystyrene	20,400	acetone	UCST	0.01216	-0.120
Polystyrene	37,000	isopropylacetate	LCST	-21.50510	48.713
Polystyrene	110,000	isopropylacetate	LCST	-8.07881	19.076
Polyisobutylene	227,000	diisobutylketone	UCST	0.04889	-0.124

Experimental data are from Ref. [14].

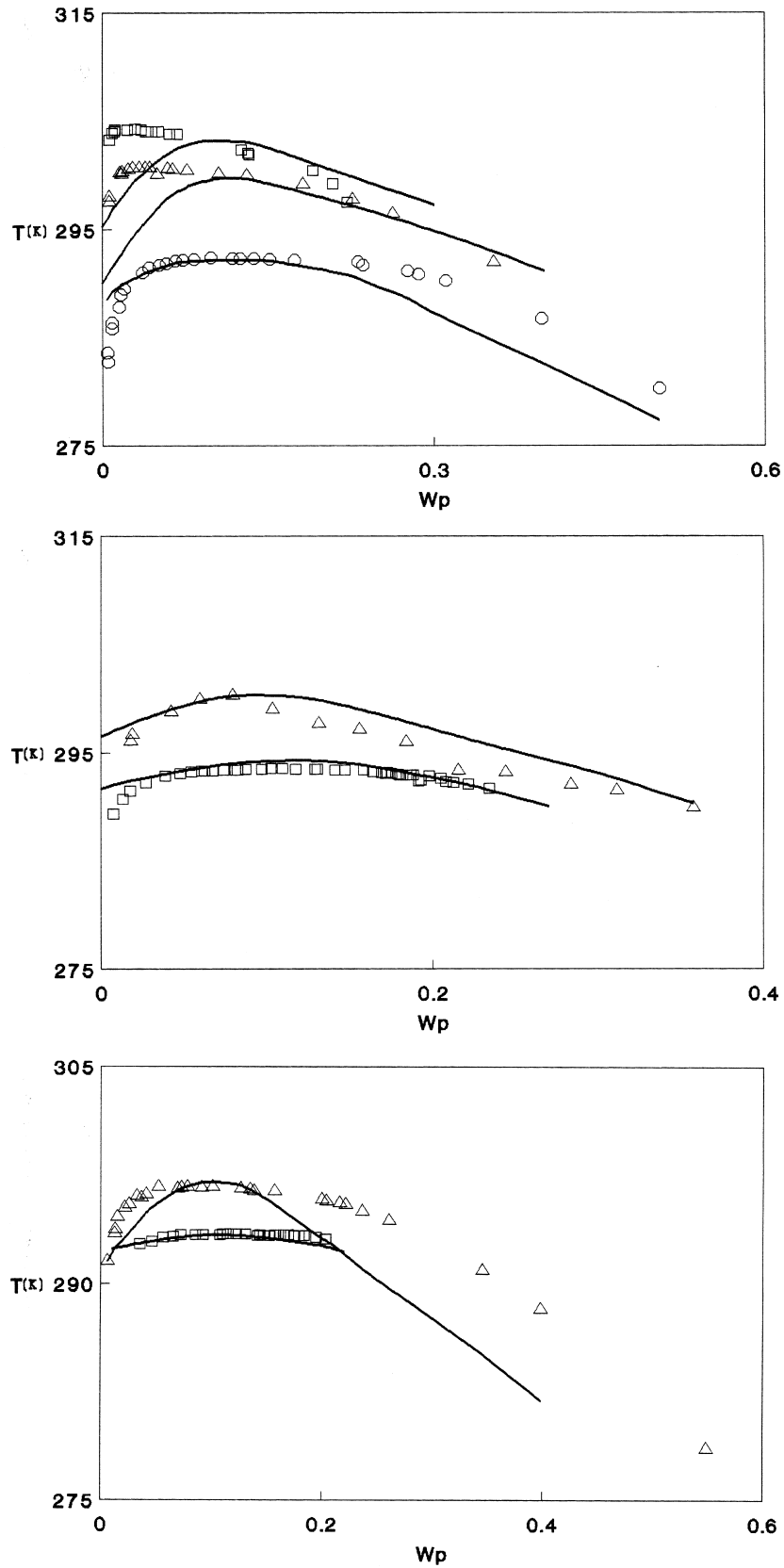


Fig. 5. (a) Effect of molecular weight of polymer for polystyrene/cyclohexane on UCST. a_{ij} and b_{ij} are various in each systems which have been given in Table 4. (— calculation, \square $M_w = 1,270,000$, \triangle $M_w = 250,000$, \circ $M_w = 43,600$.) (b) Effect of molecular weight of polymer for polystyrene/cyclohexane on UCST. a_{ij} and b_{ij} are various in each systems which have been given in Table 4. (— calculation, \square $M_w = 97,130$, \triangle $M_w = 80,000$.) (c) Effect of molecular weight of polymer for polystyrene/cyclohexane on UCST. a_{ij} and b_{ij} are various in each systems which have been given in Table 4. (— calculation, \square $M_w = 97,000$, \triangle $M_w = 89,000$.)

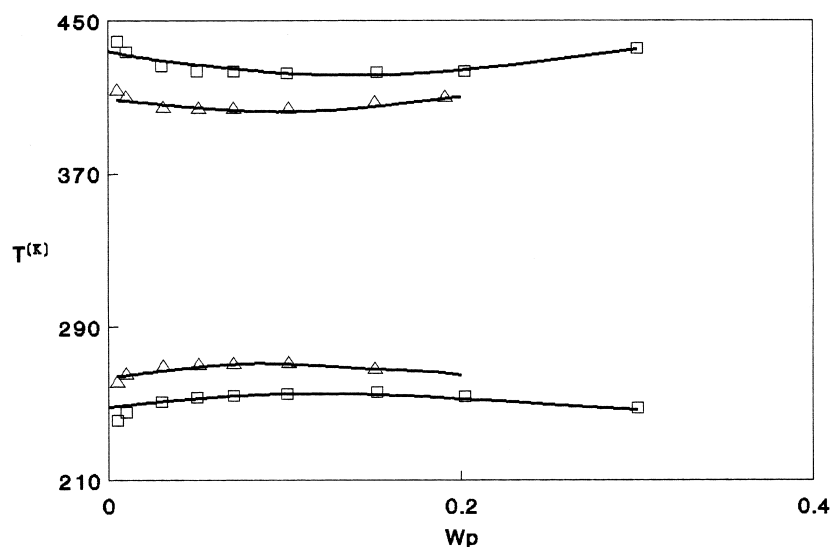


Fig. 6. Cloud point temperatures as a function of polymer weight fraction for polystyrene/*tert*-butylacetate. Effect of molecular weight of polymer on UCSTs and LCSTs that in each systems a_{ij} and b_{ij} are various. (— calculation, \square $M_w = 100,000$, \triangle $M_w = 233,000$.)

0.02237 [10]. This parameter is considered negligible for high molecular weight compounds and polymers compared to the second term of Equation (14). As the polymer solutions, studied in this work contain solvents which include -O-, -COO-, $\text{CH}_3\text{-CO-}$ groups, the first step is to examine the accuracy of the values reported [10, 14] for group contribution parameters for series of low molecular weight compounds. Thus the vapor pressure of solvents and weight fraction activity coefficient values in polymer solutions should be as reported in Tables 2 and 3. These tables show the superiority of the new parameters in correlating vapor pressure of solvents and VLE of polymer solution over the old parameters.

LIQUID-LIQUID EQUILIBRIA IN POLYMER SOLUTIONS

The basis of the phase equilibrium and stability condition in any system, including molecular and polymer solutions, is the minimization of the total Gibbs free energy of the system with respect to the system equilibrium variables. However, it has been customary to use the equality of chemical potentials condition for phase equilibrium calculation of molecular solutions. This condition, in principle, is a necessary but not sufficient condition for the Gibbs free energy minimization. While the equality of chemical potentials condition has been a useful short-cut method for phase equilibrium calculation for the GCLF equation of state it seems more

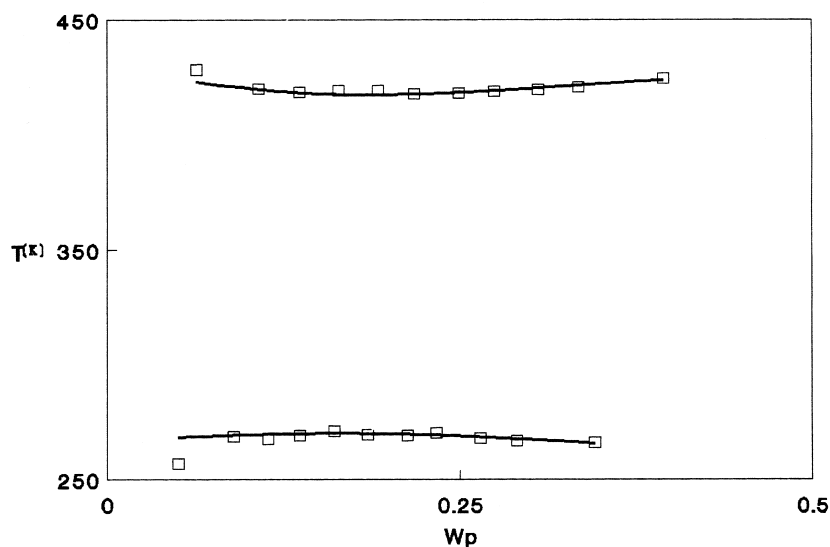


Fig. 7. Cloud point temperature as a function of polymer weight fraction for polystyrene/acetone ($M_w = 10300$). (— calculation, \square expt. data.)

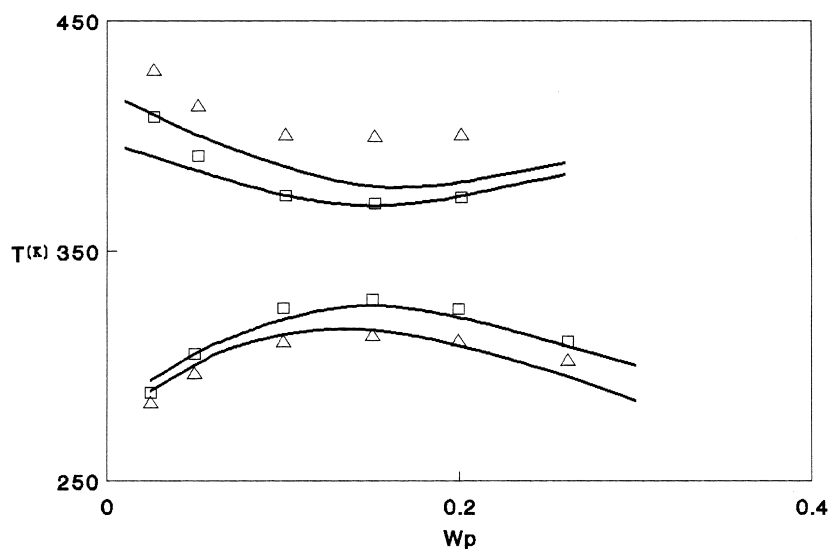


Fig. 8. Effect of pressure on LCST and UCST for polystyrene/acetone system ($M_w = 20400$). a_{ij} and b_{ij} are equal for each cloud point curves (LCST, UCST) for different cloud curves (LCST, UCST) a_{ij} , b_{ij} are various. (— calculation, \square 20 bar, \triangle 50 bar.)

suitable to use area methods based on the Gibbs free energy.

Recently, an area method [11,12] is formulated for phase equilibrium calculation, which is based on integrating the Gibbs free energy surface. The area method provides the necessary and sufficient conditions for the total Gibbs free energy minimization, rather than only the necessary condition provided by the equality of chemical potentials [11,12]. In the present report we adopt this area method for polymer solutions phase equilibrium calculation through a numerical scheme.

For the two phases (I and II) to exist in equilibrium, they must satisfy the following thermodynam-

amic conditions.

$$P^I = P^{II} \quad \text{and} \quad T^I = T^{II} \quad (17)$$

$$\delta G_{\text{total}} = \delta(G_I + G_{II}) \geq 0 \quad (18)$$

Where P is the total pressure, T is the absolute temperature, and δG_{total} represents the virtual displacement of the total Gibbs free energy of the two-phase system from equilibrium. Solution of the above three conditions can result in calculation of compositions of the two phases in equilibrium.

In order to perform liquid-liquid equilibrium calculations by the area method, the specific (per unit mass) Gibbs free energy of mixing

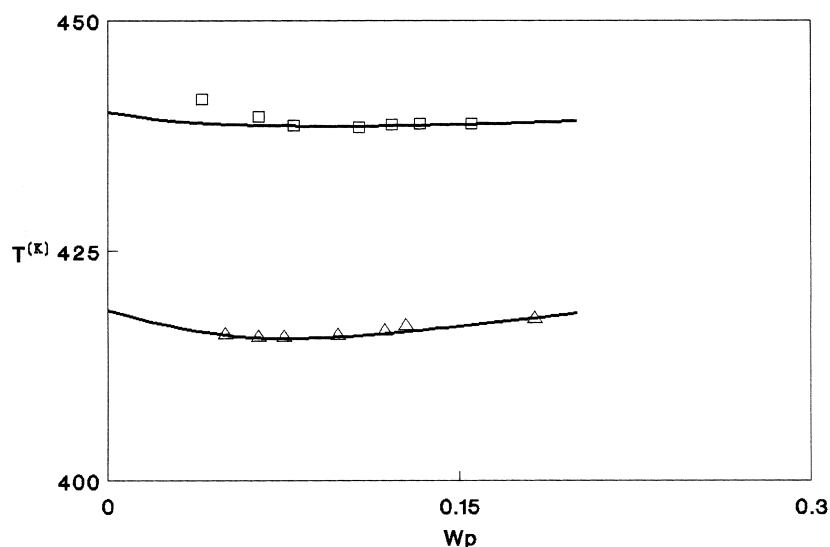


Fig. 9. Effect of molecular weight of Polymer for polystyrene/isopropylacetate on LCST curves. (— calculation, \square $M_w = 37,000$, \triangle $M_w = 110,000$.)

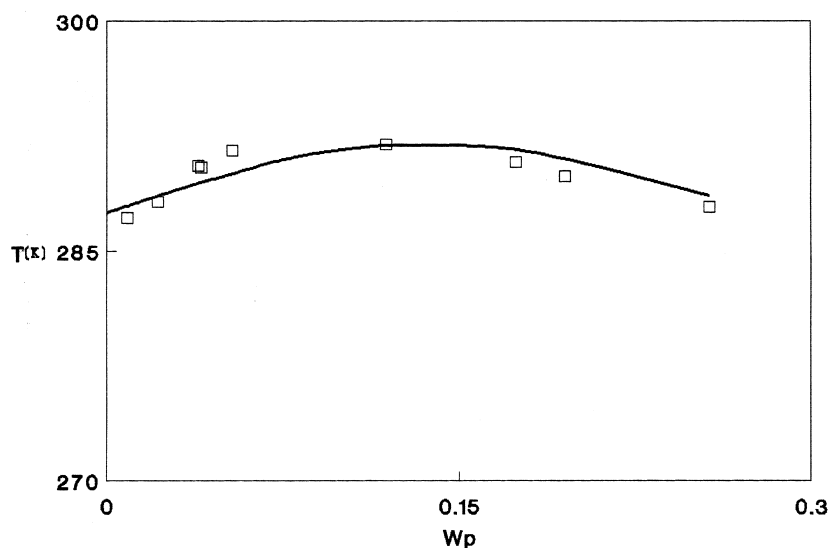


Fig. 10. Cloud point curve (UCST) for polyisobutylene/diisobutylketone ($M_w = 227000$). (— calculation, \square expt. data.)

$$(\Delta G)_{m,sp} = RT \sum \frac{w_i}{Mw_i} \ln a_i \quad (19)$$

at fixed temperature, T , and pressure, P , against weight fraction of component i , w_i , are plotted. Equation (2) is used to calculate the activity of solvent directly. So activity of polymer at a given temperature and pressure will be calculated from the Gibbs-Duhem equation.

$$\sum x_i d \ln a_i = 0 \quad (\text{at constant } T \text{ and } P) \quad (20)$$

As indicated in the preceding section, the condition for instability of a binary liquid mixture depends on the non-ideality of the solution and on the temperature. In general, it may be a maximum (upper) or a minimum (lower) temperature on a T - x diagram.

The miscibility of polymer and solvent usually increases with temperature until complete miscibility is reached at an upper critical solution temperature (UCST). If the temperature is further increased, however, the solution again becomes only partially miscible at a lower critical solution temperature (LCST).

RESULTS AND DISCUSSION

To obtain the molecular parameters, the vapor pressure and specific volume of liquid for each pure substance is used in Equation (1) on a wide range of temperature. Then the molecular parameters are inserted in Equations (14) and (15). By using linear and nonlinear regression methods the group parameters are calculated and the results are reported in Table 1. As it is seen in this table some of the calculate group contributions are reported for the first time. The others are improved and can be compared with their previous values. To examine the accuracy of the group contribution values reported in Table 1, they are used to calculated vapor press-

ure and as it is seen from Table 2 the percentage error is reduced to an average less than 37%. It is worth noting that improving the $\text{CH}_3\text{-CO-}$ group parameters causes to obtain more accurate results from equation of state.

The vapor-liquid equilibria calculations are performed using the GCLF equation of state for polymer-solvent systems. The calculations done on vapor-liquid equilibria for acetone-benzene, Fig. 1, indicate that the results are improved when the new values for the group parameters in acetone are used. For this system, the adjustable parameter k_{ij} in Equation (12) is equal to zero.

$$\% \text{AveError} = 100 \cdot \frac{\sum |(\text{Cal.} - \text{Exptl.})/\text{Exptl.}|}{n}$$

In Table 3 the activity coefficients calculated using Equation (2) for several polymer-solvent systems are reported. In comparison with the experimental data, it is seen from this stable, that they have been improved when new group values are used in the equation of state.

The liquid-liquid equilibrium calculations are performed using Equations (1)-(16) and by application of the area method. The results are shown in Figs 2, 3, 4, 5, 6, 7, 8, 9 and 10. The adjustable parameters of Equation (13) are reported for each polymer-solvent system in Table 4.

Figure 2 is the cloud point curve for ethylacetate/polystyrene systems. According to this figure the experimental data is well fitted to the calculated data and the predicted LCST is in good agreement with the experimental data. Also in this figure it is shown that the calculated LCST curve with $k_{ij}=0$ for polymer solution have a large deviation with experimental data.

In Fig. 3 is shown the system of polystyrene in methylacetate with $M_w = 179300$. According to this figure it is seen that the method can predict UCST for this system quite well.

Figure 4 shows the behavior of methylcyclohexane/polystyrene system for different molecular weight of polymer. For this system only UCSTs were detected. The calculated results are in agreement with the experimental data. Figure 5(a, b, c) show the systems of cyclohexane/polystyrene. According to these figures the experimental data and calculated results for the UCST are in good agreement. Also in these figures the effect of polymer molecular weight on the cloud point curves are shown. Figure 6 shows the effect of polymer weight fraction on the phase diagram of the system tert-butylacetate/polystyrene. According to this figure, both, experimental and calculated UCST and LCST are in agreement.

Figure 7 shows the comparison of calculated curves and experimental data where the LCST and UCST calculations for acetone/polystyrene are shown to fit well with the experimental data. In the Fig. 8 the effect of pressure on LCST and UCST are shown. It is seen that while the variation of LCST and UCST have the right trend, the a_{ij} and b_{ij} in Equation (13) are pressure independent.

As pressure increases, the GCLF equation of state predicts an increase in the LCST and a decrease in the UCST which are smaller than the changes seen in the experimental data (see Fig. 8). Since equation of state does not show adequate pressure dependency of the critical solution temperatures. Figure 9 shows the cloud point curves for isopropylacetate/polystyrene mixture. For this system also the calculated LCST curves are in good agreement with the experimental data.

Figure 10 is for polyisobutylene in diisobutylketone where UCST curve, is in agreement with the experimental data.

CONCLUSION

The application of the GCLF equation of state is highly dependent on the availability of accurate group parameter values. Extensive amount of calculation were performed to obtain accurate values for various group parameters using pure polymer vapor pressure data and polymer-solvent mixture activity coefficient data.

The GCLF equation of state originally proposed was used for the VLE prediction polymer-solvent systems. In this paper the applicability of the GCLF equation of state is extended also for the LLE prediction of polymer-solvent mixtures. In order to apply the GCLF equation of state for accurate LLE prediction it is necessary to introduce a combining rule with an adjustable parameters for the energy parameter of each polymer-solvent systems. The model developed from this study predicts the experimental LCST and UCST (cloud point) temperatures of various polymer-solvent systems with good accuracy.

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