Influence of the Alkyl Tail on the Solubility of Poly(alkyl acrylates) in Ethylene and CO$_2$ at High Pressures: Experiments and Modeling

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ABSTRACT: Cloud point data to 230°C and 2200 bar are presented for poly(acrylate)–ethylene mixtures. When the length of the alkyl tail is increased, the cloud point curve is shifted towards lower pressure, but this trend switches when going from poly(ethyl hexyl) to poly(octadecyl) acrylate. It is apparent that there is an optimum alkyl tail length that balances energetic acrylate–acrylate, ethylene–ethylene, and ethylene–acrylate interactions and free-volume, entropic effects. Both ethylene–poly(acrylate) and CO$_2$–poly(acrylate) data are modeled by the Statistical Associating Fluid Theory (SAFT) equation of state. A pseudogroup contribution method is developed for the calculation of the following pure polymer characteristic parameters: m, the number of segments, and v^{00}, the volume of a segment. This method cannot be applied for u^0/k, the attractive energy of a segment, which changes in a nonlinear manner with changes in the structure of the acrylate repeat group. The energy parameter is then calculated from monomer data or fitted directly to one cloud point curve. The experimental data are represented well, even if little predictive power is obtained since a temperature-independent interaction parameter k_{ij} is needed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1979–1991, 1999

Key words: high-pressure phase behavior; polyacrylates; supercritical fluids; modeling; Statistical Associating Fluid Theory equation of state

INTRODUCTION

One class of statistically random copolymers that is finding widespread application are copolymers that combine nonpolar ethylene with a variety of polar comonomers, such as acrylates, vinyl acetate, and acids. Ethylene-based copolymers are typically produced at pressures as high as 2000 to 3000 bar and at temperatures as high as 250°C.[1]

Elevated pressures are needed to maintain a single phase during copolymerization. It is important to know the location of the phase boundaries for copolymer–ethylene mixtures to avoid reactor fouling or runaway reactions that can occur if a two-phase region is formed in the reactor. Quite a large data base has recently emerged on the phase behavior of ethylene-based copolymers, showing that the location of the cloud point curve is a nonlinear function of the copolymer properties, such as molecular weight, degree of chain branching, and, most importantly, polar comonomer content.[2–24] In addition, the phase behavior of ethylene-based copolymers is also a strong function of the particular polar comonomer, even for comonomers from the same chemical family.

For instance, it has been shown that cloud point pressures for ethylene–methyl acrylate copolymers in ethylene decrease as the first 20 mol % of methyl acrylate groups are added to polyethylene.[3] The cloud point pressures then increase as more methyl acrylate is added to the backbone of the copolymer. In contrast, the cloud point pressures for ethylene–butyl acrylate copolymers in ethylene consistently decrease as the butyl acrylate content increases.[3] To aid in the interpretation of the phase behavior of ethylene–acrylate copolymers, the phase behavior of poly(acrylate)–ethylene mixtures is determined since the poly(acrylates) represent the polar end of the composition spectrum of ethylene–acrylate copolymers.

Cloud point data are presented for ethylene with poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(butyl acrylate) (PBA), poly(2-ethyl-hexyl acrylate) (PEHA), and poly(octadecyl acrylate) (PODA). These data complement an earlier study, which reported on the cloud point behavior of the same polymers in supercritical CO_2.[23] PEA, PBA, PEHA, and PODA dissolve in CO_2 at pressures near 1000 bar, but each cloud point curve exhibits a sharp increase in pressure at a given temperature that decreases as the length of the alkyl tail on the acrylate decreases. The sharp pressure increase is related to the strength of the polar interactions between the dipole of an acrylate group and the quadrupole of CO_2. The effective dipole of the acrylate group scales inversely with the square root of the molar volume,[25] which means that as the alkyl tail decreases, favorable CO_2–acrylate polar interactions are enhanced. It should also be noted that the ordering of the poly(acrylate) cloud point curves in pressure–temperature space was not fixed by the polymer molecular weight in this instance.

Ethylene is expected to exhibit some of the solvent characteristics of CO_2 since ethylene also has a quadrupole moment. Byun et al.[3] reported that the cloud point curve for the PBA–ethylene system is relatively flat at ∼ 800 bar and temperatures from 65 to 190°C. The behavior of the PBA–ethylene system is similar to that of the PBA–CO_2 system, where the curve is flat at ∼ 1000 bar from 130 to 200°C.[23] However, as previously mentioned, the PBA–CO_2 curve has a sharp increase in pressure at ∼ 80°C, whereas the PBA–ethylene curve is still flat at this temperature.[23] PBA remains dissolved in ethylene to lower temperatures because ethylene has a much higher polarizability than CO_2, 42.5 cm^3 versus

Table I Molecular Weight Information for the Polymers Investigated in this Study

Polymer	M_w	M_w/M_n
Poly(methyl acrylate) (PMA)	30,700	2.90
Poly(ethyl acrylate) (PEA)	119,300	4.83
Poly(butyl acrylate) (PBA)	61,800	2.99
Poly(ethylhexyl acrylate) (PEHA)	112,800	2.97
Poly(octadecyl acrylate) (PODA)	23,300	1.79
Poly(butyl methacrylate) (PBMA)	102,300	1.02
Poly(vinyl acetate) (PVAc)	124,800	2.37
EMA$_{18}$[a]	185,200	4.90
EMA$_{31}$	99,000	3.00
EMA$_{41}$	96,400	3.22

[a] EMA$_x$ is a poly(ethylene-*co*-methyl acrylate) copolymer with *x* mole percent of methyl acrylate in the backbone.

27.5 cm^3, and, therefore, PBA–ethylene dispersion interactions, are much stronger. Dispersion interaction energy scales with polarizability divided by molar volume, which explains why high pressures are needed for ethylene and CO_2 to dissolve PBA since these solvents are expanded gases at elevated temperatures and ambient pressure.

Table I lists the properties of the poly(acrylates) used in this study. Although the molecular weights of the polymers are not identical and the polydispersities are relatively high, these two properties should not be primary factors controlling the location of the cloud point curve based on observations from other polymer–supercritical fluid solvent studies.[3,14] SAFT is used to model the ethylene–poly(acrylate) cloud point data obtained in this study and the CO_2-poly(acrylate) data reported elsewhere.[23] The Radosz group has used the SAFT model extensively to calculate the phase behavior of polymer–solvent mixtures.[4,6,8–10,26,27] A straightforward method is proposed for calculating the pure component parameters of the poly(acrylates) based on the parameters of low-molecular-weight propanoates that are homomorphs of the acrylate repeat groups.

EXPERIMENTAL

Described in detail elsewhere are the techniques used to obtain cloud point curves using a high-pressure, variable-volume view cell.[18] While being maintained at room temperature, the cell is loaded with polymer and is purged to remove any

Figure 1 Impact of the acrylate alkyl tail on the cloud point curves of (△) poly(ethyl acrylate) (PEA), (□) poly(butyl acrylate) (PBA), (●) poly(ethyl hexyl acrylate) (PEHA), and (○) poly(octadecyl acrylate) (PODA) in ethylene obtained in this study.

entrapped air. Ethylene is then transferred into the cell. The system pressure is measured to within ±2.8 bar, and the system temperature is measured and maintained to within ±0.4°C. The cloud point pressure is defined as the point at which the solution becomes so opaque that it is no longer possible to see the stir bar in solution. Cloud points obtained in this manner are identical to those defined as the point where there is a 90% drop in transmitted light through the solution. Cloud point measurements are repeated at least twice at each temperature and are typically reproducible to within ±5 bar. The poly(alkyl acrylates) were obtained from Aldrich Chemical Co.; since they were supplied in a toluene solution, the polymer solution was placed under vacuum for at least 8 h for solvent removal. Ethylene (CP grade; 99.5% pure), obtained from Linde Corporation, and the inhibitor (2,6-di *tert* butyl-4 methyl phenol), obtained from Aldrich Chemical Company, were used as received.

RESULTS AND DISCUSSION

Phase Behavior

Figure 1 shows the phase behavior of PEA, PBA, PEHA, and PODA in ethylene. It was not possible to dissolve PMA in ethylene to pressures up to 2500 bar and temperatures to 250°C, even though PMA has a very low-weight average molecular weight. More than likely, PMA remains insoluble in ethylene due to methyl acrylate segment–seg-

ment polar interactions that are much stronger than acrylate segment–ethylene interactions.

PEA dissolves in ethylene at pressures near 1200 bar and temperatures in excess of 150°C. However, as the temperature decreases, the PEA–ethylene curve exhibits a gradual increase in pressure to 2200 bar at 50°C, which suggests that polar ethyl acrylate–ethyl acrylate interactions also gradually increase over this temperature range. As the length of the alkyl tail on the acrylate increases from methyl to ethyl, the impact of the polar acrylate interactions decreases since dipolar interactions scale inversely with the square root of the molar volume and quadrupolar interactions scale inversely with the volume to the 5/6 power.[25]

Figure 1 shows that it takes less pressure to dissolve PBA compared to PEA. In fact, the cloud point curve for the PBA–ethylene system remains relatively flat at 800 bar from 175 to 60°C. Evidently, the butyl tail reduces the impact of polar interactions sufficiently to suppress strong butyl acrylate–butyl acrylate interactions so that the cloud point curve does not exhibit an increase in pressure as was observed with the PEA–ethylene system.

Note that the PEHA–ethylene cloud point curve is flat at 680 bar from 100 to 200°C, but it exhibits a positive slope that decreases from 680 to 500 bar as the temperature decreases from 100 to 30°C. As the acrylate tail is increased from ethyl–hexyl to octadecyl, the cloud point curve increases in pressure and virtually superposes on the PBA–ethylene curve. It appears that there is an optimum alkyl tail length that balances the acrylate–acrylate, ethylene–ethylene, and acrylate–ethylene energies of this system. However, increasing the tail length of the acrylate group is also expected to increase the free volume of the poly(acrylate), which makes it easier to dissolve in highly expanded, supercritical ethylene. PODA should have a higher free volume than PEHA, but the balance of PODA–ethylene interactions is probably less favorable than that of PEHA–ethylene since the polar character of the octadecyl acrylate is spread over such a large volume. Both energetic and entropic effects need to be considered when interpreting the phase behavior for these systems.

Relative to CO_2, ethylene is a better supercritical solvent for the poly(acrylates). The PODA cloud point curves for these two systems exhibit perhaps the most striking difference in phase behavior. The PODA–CO_2 curve increases abruptly

in pressure at approximately 230°C,[23] while the PODA–ethylene curve remains flat to temperatures as low as 20°C. As mentioned earlier, both CO_2 and ethylene have quadrupole moments; but ethylene has a much higher polarizability, which makes it much better solvent than CO_2 for hydrocarbon polymers. The important question is whether the Statistical Associating Fluid Theory (SAFT) can recognize the difference between these two important supercritical fluid solvents.

Modeling

SAFT is used to calculate the phase behavior for the poly(acrylate)–ethylene mixtures considered in this study and for the poly(acrylate)–CO_2 mixtures reported previously.[23] SAFT is a perturbation equation of state developed by Chapman et al.,[28] who applied the theory of associating fluids developed by Wertheim.[29–32] Molecules are represented as covalently bonded chains of segments, which may contain sites capable of forming associative complexes. In SAFT, the reference Helmholtz free-energy terms account for the connectivity of the hard segments in the main chain, a^{chain}, the hard-sphere repulsion of the segments, a^{hs}; and the energy of site-site specific interactions of the segments with themselves or other segments, a^{assoc}, and the perturbation term consists of a mean-field attractive term, a^{disp}. The residual Helmholtz free-energy, a^{res}, relative to the ideal gas reference state is

$$a^{res} = (a^{hs} + a^{chain} + a^{assoc}) + a^{disp} \qquad (1)$$

The term for the energy of association or complex formation is set equal to zero since the poly(acrylates), ethylene, and CO_2 are not expected to self- or cross-associate. In the calculations presented here, the polymer molecular weight is assumed to be monodisperse, since this assumption is not expected to mask the large changes observed in the phase behavior with changes in acrylate structure. The cloud point curves are obtained by calculating pressure–composition (P–x) isotherms at various temperatures and identifying the cloud point pressure as the pressure needed to obtain a single phase at 5 wt % polymer in solution.

The expression for the residual Helmholtz free energy, given in detail elsewhere,[26,27] is used, along with thermodynamic definitions, to derive an equation for the fugacity coefficient, ϕ_i, to calculate phase equilibria.

$$\ln \phi_i = \frac{\mu_i^{res}}{RT} - \ln Z \qquad (2)$$

where Z is the compressibility of the mixture, R is the gas constant, T is the temperature, and μ_i^{res} is the residual chemical potential that is defined as

$$\frac{\mu_i^{res}}{RT} = \left(\frac{\partial (Na^{res}/RT)}{\partial N_i} \right)_{T,V,N_{j\neq i}} \qquad (3)$$

where N is the total number of moles in the system, V is the total system volume, and N_i is the number of moles of component i in the system. Equation (2) can be rewritten in terms of the residual Helmholtz energy as

$$\ln \phi_i = \left\{ \frac{\partial \left[\frac{a^{res}}{RT} \right]}{\partial x_i} \right\}_{T,V,N_{j\neq i}} - \sum x_j \left\{ \frac{\partial \left[\frac{a^{res}}{RT} \right]}{\partial x_j} \right\}_{T,V,N_{j\neq i}}$$
$$+ a^{res}/RT + (Z - 1) - \ln Z \qquad (4)$$

where x_i is the mole fraction of component i (see Huang and Radosz[26] and Hasch[33] for more details).

For each pure component, there are potentially five parameters in the SAFT equation, as follows: v^{00}, the temperature-independent volume of a segment; u^0/k, the temperature-independent, nonspecific energy of attraction between two segments; m, the number of segments in a molecule; ε/k, the energy of association between sites on a molecule, and v, the volume of site–site association. For the systems considered here, ε/k and v are zero since there are no hydrogen-bonding molecules present. The following three mixing rules are needed to calculate the phase behavior for mixtures: one for the temperature-dependent volume of a segment, v^0; another for the temperature-dependent energy of attraction between two segments, u; and a third one for the number of segments, m. The mixing rules are

$$v^0 = \frac{\sum_i \sum_j x_i x_j m_i m_j v_{ij}^0}{\left[\sum_i x_i m_i \right]^2}$$

where

$$v_{ij}^0 = \frac{1}{8} \left[v_i^0 \frac{1}{3} + v_j^0 \frac{1}{3} \right]^3 \qquad (5)$$

Table II   Parameters Used in the SAFT Modeling

Component	m	v^{00} (cm³/mol)	$(u^o/k)_{\mathrm{Pvap}}$ [a]	$(u^o/k)_{\mathrm{CP}}$ [b]
CO_2	1.417	13.578	216.08	—
Ethylene	1.464	18.157	212.06	—
Methyl acrylate	4.928	8.626	209.0	—
Vinyl acetate	4.928	8.626	203.0	—
Butyl acrylate	6.890	9.540	205.0	—
PMA	592	9.193	209.0	240.0
PEA	1348	9.509	205.0	215.0
PBA	1093	9.958	205.0	203.0
PEHA	1973	10.956	195.5	198.0
PODA	638	11.034	—	200.0
PBMA	5238	10.124	202.0	208.0
PVAc	2941	9.193	203.0	225.0

[a] u^o/k (K) for the polymer is calculated from monomer vapor pressure and liquid density data.
[b] u^o/k (K) for the polymer is fit to the polymer–ethylene cloud point curve.

$$\frac{u}{kT} = \frac{\displaystyle\sum_i \sum_j x_i x_j m_i m_j \left[\frac{u_{ij}}{kT}\right] v_{ij}^0}{\displaystyle\sum_i \sum_j x_i x_j m_i m_j v_{ij}^0}$$

where

$$u_{ij} = (u_{ii}u_{jj})^{1/2}(1 - k_{ij}) \tag{6}$$

$$m = \sum_i \sum_j x_i x_j m_{ij}$$

where

$$m_{ij} = \tfrac{1}{2}(m_i + m_j) \tag{7}$$

The parameter k_{ij} is a fitted, binary mixture parameter.

Parameters for Pure Components

Table II lists values for the pure component parameters v^{00}, u^o/k, and m for ethylene and CO_2 reported elsewhere.[26] The pure component parameters for the poly(acrylates) are not available in literature. The challenge associated with determining reasonable pure component polymer parameters is demonstrated for the PEA–ethylene system. The pure component parameters for PEA, obtained from a fit of density data[34] to within 2%, are 17.17 cm³/mol for v^{00}, 778.5 for m, and 367.4 K for u^o/k. With these values and k_{ij} set equal to zero, the calculated cloud point curve is more

than 7000 bar too high relative to the experimental curve. If k_{ij} is set equal to -0.150, a large negative value, a portion of the cloud point curve is now close to the experimental data, but the calculated curve has a positive slope indicative of lower critical solution temperature (LCST) behavior, while the experimental curve has a negative slope. The primary reason that cloud point calculations are so far off in this instance is that the value of u^o/k is much too large, as has already been noted by others.[35,36] As Figure 2 shows, the calculated density of PEA is not very sensitive to the value of u^o/k, which renders this data of little value when determining pure component polymer parameters. It is apparent that another method is needed to calculate the three polymer pure component parameters.

Figure 2   Influence of u^o/k on the calculated density of poly(ethyl acrylate). The open circles are densities obtained from the Tait equation.[34]

Determination of the Number of Segments and of the Volume of a Segment

Huang and Radosz[26] argue that the parameters m and v^{00} for polyethylene can be obtained by extrapolating the results found with n-alkanes parameters; moreover, they show that the values for m and v^{00} follow regular trends, depending on the structural features of the species under consideration. The approach taken here to determine polymer pure component parameters follows from the observations of Huang and Radosz,[26] which suggest that a group contribution method can be used for their determination. The basic assumption in the group contribution approach is that the values of m and m times v^{00} can be obtained from the linear summation of the values for each functional group in the molecule. The values of m and v^{00} for polymers is obtained from the values for a repeat unit and with m corrected for the size of the polymer utilizing the number-average molecular weight.

The number of segments m for a repeat unit of a particular poly(acrylate) is determined by first calculating m for the base ester group, CH_3—CH_2COO—, from the values given for a series of propanoates[26] minus the contribution of the —CH_2— and —CH_3 groups that constitute the alkyl tail on the propanoate. The value of m for the acrylate group in the backbone of the polymer without an alkyl tail is then obtained by subtracting m for a —CH_2— group from the m of the ester group and adding m for a >CH— group. The m for a particular alkyl tail is calculated by summing the m values of the appropriate number of —CH_2— groups with the value for a —CH_3 group. For simplicity, no attempt is made to account for the type of functional groups pendant to the CH_2 group. The value for m_{CH_2}, 0.654, is obtained from the slope of a plot of $m_{n\text{-alkanes}}$[26] versus the number of carbon atoms. The value for m_{CH_3} is obtained with the following equation:

$$m(-CH_3) = \frac{m(n\text{-alkane}) - (n-2)m(-CH_2-)}{2} \tag{8}$$

Huang and Radosz[26] report $m_{n\text{-alkane}}$ values for different alkanes, which gives an average value for m_{CH_3} of 1.067. The m_{CH} value is calculated from

$$m(-CH=) = m(C_3H_6) - m(-CH_3) - m(=CH_2) \tag{9}$$

where it is assumed that an m_{CH} with three single bonds is equal to an m_{CH} with a single and a double bond and that the $m_{CH_2=}$ is one-half that of $m_{ethylene}$. Values for $m_{ethylene}$ and $m_{propylene}$ are found elsewhere.[26]

The value for the product of m times v^{00} for a repeat group of a given poly(acrylate) is obtained using the same approach as that used to obtain m of the repeat group. Specifically, eqs. (8) and (9) are used, except that the m_{group} is replaced with the product mv^{00}_{group}. Once mv^{00} is calculated for the repeat group of the poly(acrylate), v^{00} is then calculated with the following equation:

$$(v^{00})_{group} = \frac{(mv^{00})_{group}}{m_{group}} \tag{10}$$

The value for m for a given poly(acrylate) is obtained by multiplying $m_{acrylate\ segment}$ by the poly(acrylate) number-average molecular weight and dividing by the molecular weight of the acrylate repeat group.

This group contribution approach is also used to determine the pure component parameters for acrylate monomers. The value of m for the acrylate group (ACgr), which contain a double bond but does not have an alkyl tail, is obtained from the following equation:

$$m(ACgr) = m(ESTgr) - m(-CH_3)$$
$$- m(-CH_2-) + m(=CH_2) + m(+CH-) \tag{11}$$

where ESTgr is the ester group. The contribution of the appropriate alkyl tail is added similarly to the manner used for the acrylate repeat group in a poly(acrylate), and v^{00} is also determined in the manner used for the acrylate repeat group.

Determination of the Energy Parameter

Unfortunately, the energy parameter of a segment, u^0/k, within a particular chemical family, varies in a nonlinear manner with respect to the group carbon number, which precludes using a simple group contribution method for estimating it. Given values of m and v^{00} obtained from the group contribution method, the following three different approaches are possible to determine a value for u^0/k of a poly(acrylate) segment.

1. A fit of poly(acrylate) density data can be used;
2. u^0/k can be calculated for the monomer

Figure 3 Comparison of the experimental butyl acrylate–CO_2 phase behavior[40] with isotherms calculated with the SAFT equation using the pure component parameters shown in Table II and with k_{ij} equal to 0.130.

from a fit of vapor pressure and liquid density data, and then used for the corresponding polymer; in this case, it is also possible to determine a value of k_{ij} from a fit of monomer–solvent phase behavior data, which can be used for the polymer-solvent calculations;

3. A single poly(acrylate)–solvent cloud point curve for a given solvent can be used to determine u^0/k for the polymer and k_{ij} for the polymer–solvent pair.

For the possible poly(acrylate)–ethylene and poly(acrylate)–CO_2 mixtures considered in this study, all three types of data are available only for the PBA–CO_2 system. Therefore, the merits of these three approaches will be demonstrated with the PBA–CO_2 system, and then further examples are provided for the poly(acrylates)–ethylene, poly(acrylates)–CO_2, and poly(vinyl acetate)–CO_2 systems.

Example Calculation of u⁰/k for Butyl Acrylate

In the first approach, u^0/k for PBA, 320.0 K, is determined from a fit of PBA density data, with m and v^{00} calculated from the group contribution method. With these pure-component PBA parameters, the calculated PBA–CO_2 cloud point pressures are approximately 5000 bar too high. Again, it is found that polymer density data are not useful for regressing the energy parameter; therefore, this approach is discarded.

In the second approach, $m_{\text{butyl acrylate}}$, 6.772, and v^{00}, 9.958 cm^3/mol, are obtained from the

group contribution equations, and a value of 205.0 K is obtained for $u^0/k_{\text{butyl acrylate}}$ from a fit of butyl acrylate vapor pressure data to within $\pm 1.8\%$ and butyl acrylate liquid density data[37] to within $\pm 6.4\%$. Figure 3 shows a comparison of calculated and experimental phase behavior of the butyl acrylate–CO_2 system using these parameters. Poor agreement between calculated and experimental isotherms is obtained with k_{ij} equal to zero, although more quantitative fits of these isotherms are obtained with k_{ij} equal to 0.130.

Figure 4 shows a comparison of the calculated and experimental cloud point curves for the PBA–CO_2 system. With u^0/k for PBA equal to that of the monomer and k_{ij} equal to zero, the calculated cloud point curve exhibits a positive slope that does not agree even qualitatively with the experimental curve. A quantitative fit of the data can be obtained with k_{ij} equal to 0.071. If k_{ij} is set equal to 0.130, the value found from the best fit of the butyl acrylate–CO_2 system, the PBA cloud point curve pressures are too high, and the sharp pressure increase of the calculated curve is shifted to higher temperatures by more than 250°C.

When the third approach is used, that is, adjusting both the value of u^0/k_{PBA} and k_{ij} to obtain a good fit of the PBA–CO_2 cloud point curve, essentially identical values of u^0/k_{PBA}, 203.0 K, and k_{ij}, 0.073, are obtained compared to those found from a fit of pure monomer data. It should be emphasized that the shape and location of the

Figure 4 Comparison of the PBA–CO_2 and the PBA–ethylene experimental and calculated cloud point curves. The PBA–CO_2 data are obtained from the literature[23] and the PBA–ethylene data are obtained in this study. The value for $(u^0/k)_{\text{PBA}}$ used for both systems is obtained from a fit of monomer butyl acrylate data.

Figure 5 Comparison of the PMA–CO$_2$ calculated and experimental[23] cloud point curves with $(u^0/k)_{PMA}$ obtained from a fit of monomer vapor pressure and liquid density data.

PBA–CO$_2$ cloud point curve is very sensitive to the value of k_{ij}, as shown in Figure 4. Nevertheless, the group contribution approach advocated here provides a systematic way to determine the number of segments and the segment volume for poly(acrylates) not previously considered. The pure component parameters for PBA are now fixed and can be used with any other PBA–solvent mixture. Figure 4 also shows that a good fit of the PBA–ethylene cloud point curve is found with the value of u^0/k obtained from monomer data and with k_{ij} equal to 0.043. Further examples of the group contribution approach and the two methods to determine u^0/k are provided for the poly(acrylate)–ethylene and poly(acrylate)–CO$_2$ systems and for the poly(vinyl acetate)–CO$_2$ system, which provides a stringent test of the methodologies proposed here.

Poly(acrylate)–SCF Phase Behavior

Figure 5, which shows the PMA–CO$_2$ cloud point curve, is an example where the calculation of u^0/k_{PMA} from the vapor pressure and density of the monomer leads to unsatisfactory results. The calculated results are again extremely sensitive to the value of k_{ij}, where larger values of k_{ij} shift the cloud point curve to higher pressures and temperatures and changes the characteristics of the curve from one with a positive slope (LCST-type behavior) to one with a negative slope (UCST-type behavior). The u^0/k value obtained from methyl acrylate data, 209.0 K, is much too low to model this system. Figure 6 shows that a good representation of the cloud point curve is

obtained when u^0/k, 240.0 K, and k_{ij}, 0.043, are fit simultaneously to the cloud point curve. In this case, where the polarity of the polymer is much higher than that of the monomer, another term is needed in SAFT to explicitly account for polarity.

Figure 6 also shows that a semiquantitative fit of the PVAc–CO$_2$ cloud point curve data can be obtained with u^0/k calculated from the vapor pressure of the vinyl acetate, 203.0 K, and with k_{ij} equal to 0.055. A more quantitative fit is obtained with a higher value of u^0/k, 225.0 K, and with a k_{ij} equal to 0.020. The higher value of u^0/k may be a consequence of the polar interactions expected between vinyl acetate and CO$_2$ and the weak complex that is expected to form between the carbonyl group in vinyl acetate and CO$_2$.[38] This complex formation is most probably of a Lewis acid–base nature, where the carbon atom of the CO$_2$ molecule acts as an electron acceptor and the carbonyl oxygen in the polymer acts as an electron donor, and its strength is expected to be a bit less than 1 kcal/mol. It is possible to account for the complex formation with SAFT, but at the cost of introducing two new parameters; therefore, complex formation is ignored in the calculations reported here. Meredith et al.[39] have recently reported that it is possible to discern an effect of the complex on the calculated phase behavior; however, they had to increase the strength of the complex artificially by a factor of 4 to see a quantitative effect. It should be noted that PMA and PVAc repeat units have the same chemical formula but different structures, which makes the volume and the segment parameters equal for the two repeat units. Figure 6 shows that changing u^0/k and k_{ij} is enough to obtain a good representation of both the systems, even if, in fact, they behave very differently.

Figure 6 Comparison of PMA–CO$_2$ and PVAc–CO$_2$ calculated and experimental[23] cloud point curves.

Figure 7 Comparison of experimental[41] and calculated methyl acrylate–ethylene isotherms with SAFT and with k_{ij} equal to 0.110.

Figure 9 Comparison of the PEA–ethylene experimental cloud point curve obtained in this study with calculated cloud point curves using the SAFT equation.

Figures 7 and 8 present a comparison of experimental[41] and calculated phase behavior for the systems ethylene–methyl acrylate and ethylene vinyl acetate. A good fit of the experimental data is obtained for both of these systems with m and v^{00} obtained from the group contribution correlation and with u^0/k_{MA} and u^0/k_{VAc} determined from a fit of vapor pressure and liquid density data and with a temperature-independent k_{ij} fit to the binary phase behavior. If the calculations are performed with the values of u^0/k obtained from the polymer–CO_2 cloud point curves, the results are still in qualitative agreement with the experimental data, even with k_{ij} set equal to zero.

Figure 9 shows the fit of the cloud point curve for the PEA–ethylene system. Good agreement is

obtained between experimental and calculated cloud point curves with u^0/k, 205.0 K, obtained from the monomer data and k_{ij} fit to the cloud point curve and with both k_{ij} and u^0/k, 215.0 K, fit to the cloud point curve. The lack of a dipole term in SAFT is less severe in this instance since the dipole–dipole interactions scales with the inverse square root of the acrylate volume, which effectively reduces the impact of the ethyl acrylate dipole. The conclusion here is that the group contribution method for m and v^{00} works well with u^0/k determined from monomer data. Once again, a temperature-independent k_{ij} is needed to obtain a good representation of the cloud point curve.

Figure 10 shows the fit of the PEA–CO_2 cloud point curve where one curve uses the u^0/k from a fit of the pure monomer data, 205.0 K, while adjusting k_{ij} and the other curve uses u^0/k obtained

Figure 8 Comparison of experimental[42] and calculated vinyl acetate–ethylene isotherms with SAFT and with k_{ij} equal to 0.090. A good fit of the 60°C isotherm is also obtained, although it is not shown here to avoid clutter.

Figure 10 Comparison of the PEA–CO_2 experimental cloud point curve[23] with calculated cloud point curves using the SAFT equation.

Figure 11 Comparison of calculated and experimental cloud point curves for the PEHA–CO_2, PEHA–ethylene, PODA–CO_2, and PODA–ethylene systems. The parameters for the polymers and solvents are found in Tables II and III.

from the best fit of PEA–ethylene cloud point, 215.0 K, curve, while again adjusting k_{ij}. A reasonable representation of the PEA–CO_2 cloud point curve is obtained with the value of u^0/k obtained from monomer data, although more quantitative agreement is obtained with u^0/k regressed from the PEA–ethylene curve.

In Figure 11, experimental and calculated curves are presented for the PEHA–CO_2, PODA–CO_2, PEHA–ethylene, and PODA–ethylene systems. For PEHA, a very good representation of the experimental CO_2 curve is obtained with u^0/k fit to monomer data and with k_{ij} equal to 0.093 and for the ethylene curve with the same value of u^0/k and with k_{ij} equal to 0.045. Since monomer vapor pressure data are not available for PODA, the values for u^0/k, 200.0 K, and k_{ij}, 0.053, were obtained from a fit on the PODA–ethylene cloud point curve. The same value of u^0/k is then used for PODA–CO_2 with very good results.

In Figure 12, the PBA–CO_2 and PBMA–CO_2 systems are compared. For PBMA, a better representation is obtained from a simultaneous fit of u^0/k and k_{ij} to the cloud point curve, although a very reasonable fit of the data are obtained with u^0/k determined from monomer data.

Table III reports the values of k_{ij} used to obtain a good fit of the experimental data. For polymer–ethylene systems, k_{ij} decreases when the alkyl tail is increased, whereas the polymer–CO_2 systems show the opposite trend. For both kinds of systems, k_{ij} varies in a regular manner along the series of polymers, which makes it possible to predict its value for other components in the same homologous series.

Copolymer Systems

The group contribution method is suitable also to calculate the volume and segment parameters for statistically random copolymers once the values for each repeat unit are known. Once again, it is postulated that both m and m times v^{00} can be determined from a linear combination of those of the repeat units, weighted by the number of each repeat unit, n_i, in the backbone. For a generic random copolymer, m and m times v^{00} are

$$m_{COP} = \sum_i n_i m_i \qquad (12)$$

$$(mv^{00})_{COP} = \sum_i n_i (mv^{00})_i \qquad (13)$$

where m_i and mv_i^{00} are the segment and segment times volume parameters for each repeat unit. The number of each group in the copolymer depends on the mole fraction of each repeat unit in the copolymer and on the number-average molecular weight, as follows:

$$MW_{COP} = n_1 MW_{ru1} + n_2 MW_{ru2} \qquad (14)$$

$$x_1 = \frac{n_1}{n_1 + n_2} \qquad (15)$$

where MW_{COP} is the number-average molecular weight of the copolymer, MW_{ru} are the molecular weights of each repeat unit, and x_1 is the mole fraction of monomer 1 in the copolymer. Once the molecular weights and x_1 are known, it is straightforward to calculate n_1 and n_2.

Figure 12 Comparison of calculated and experimental[23] PBA–CO_2 and PBMA–CO_2 cloud point curves.

Table III   Values of k_{ij} for Polymer–CO$_2$ and Polymer–Ethylene Systems

Polymer	k_{ij} (polymer–ethylene)[a]	k_{ij} (polymer–CO$_2$)[a]	k_{ij} (polymer–ethylene)[b]	k_{ij} (polymer–CO$_2$)[b]
PMA	—	—	—	0.043
PEA	0.078	0.071	0.060	0.060
PBA	0.043	0.071	0.050	0.073
PEHA	0.045	0.093	0.039	0.090
PODA	—	—	0.053	0.104
PBMA	—	0.080	—	0.074
PVAc	—	0.055	—	0.020

[a] u^0/k (K) for the polymer is calculated from monomer vapor pressure and liquid density data.
[b] u^0/k (K) for the polymer is fit to the polymer–ethylene cloud point curve.

A volume-weighted, geometric-average mixing rule is used to determine the energy parameter for a given copolymer, as follows:

$$\left(\frac{u^0}{k}\right)_{COP} = \frac{\sum_i \sum_j (x_i m_i)(x_j m_j)\left(\frac{u^0}{k}\right)_{ij} v_{ij}^{00}}{\sum_i \sum_j (x_i m_i)(x_j m_j) v_{ij}^{00}} \quad (16)$$

$$u_{ij}^0 = (u_i^0 u_j^0)^{0.5} \quad (17)$$

Table IV gives values of pure component parameters for the copolymers determined with eqs. (12)–(17).

Figure 13 shows the comparison of calculated and experimental cloud point curves for the EMA$_x$–CO$_2$ system. In this instance, very good agreement is obtained between calculated and experimental data with a temperature-independent k_{ij}. Note that k_{ij} increases regularly when the amount of ethylene repeat units increases in the backbone of the copolymer. A value of 0.112 is obtained if the k_{ij} values in Figure 13 are extrapolated to polyethylene. With k_{ij} equal to 0.112

Table IV   Parameters Used in the SAFT Modeling for the Poly(ethylene-*co*-methyl acrylate) Copolymers

Copolymer[a]	m	v^{00} (cm^3/mol)	u^0/k (K)	k_{ij}
EMA$_{18}$	1903	10.654	225.9	0.048
EMA$_{31}$	1748	10.189	230.2	0.054
EMA$_{41}$	1584	9.936	232.6	0.071

[a] EMA$_x$ is a poly(ethylene-*co*-methyl acrylate) copolymer with x mole percent of methyl acrylate in the backbone.

and with parameters obtained from Huang and Radosz,[26] it is possible to show that a single phase cannot be obtained for the polyethylene–CO$_2$ system to temperatures of 270°C and pressures of 2750 bar.

CONCLUSIONS

New experimental data for poly(acrylates)–ethylene systems have been presented. The cloud point pressures for the poly(acrylates) in ethylene decreases as the length of the alkyl tail increases from methyl to *n*-ethyl hexyl. The strength of dipole–dipole interactions between acrylate groups is expected to decrease with increasing tail length since the dipole now operates over a larger volume. However, when the length of the alkyl tail increases from *n*-ethyl hexyl (PEHA) to octadecyl (PODA), the cloud point pressures also increase. These data sug-

Figure 13   Comparison of calculated and experimental[23] EMA$_{18}$–CO$_2$, EMA$_{31}$–CO$_2$, and EMA$_{41}$–CO$_2$ cloud point curves. The parameters for these calculations are given in Table III.

gest that there is an optimum alkyl tail length that balances the acrylate–acrylate, ethylene–ethylene, and acrylate–ethylene energies of this system. The change in energetics with tail length is also balanced by the increase in the free volume of the poly(acrylate) with increasing tail length, which makes these polymers easier to dissolve in highly expanded, supercritical ethylene. Both energetic and entropic effects need to be considered when interpreting the phase behavior for these systems.

The experimental data have been modeled with the SAFT equation of state using a group contribution approach to calculate m and v^{00} for the polymer and determining u^0/k from monomer vapor pressure and liquid density data or from a fit of a single polymer–solvent cloud point curve. With PMA and PVAc, the most polar polymers considered here, it is necessary to determine the value of u^0/k directly from a fit of a cloud point curve. For the other poly(acrylates), it is possible to obtain a reasonable value for u^0/k using the corresponding monomer energetic parameter. It should be noted, however, that it is necessary to use a temperature-independent binary interaction parameter k_{ij} to obtain a reasonable fit of the cloud point curves for all of the polymer–supercritical solvent systems considered here. If k_{ij} is set equal to zero, the polymer–SCF solvent curves are not even in qualitative agreement with experimentally observed values.

The predictive power of the SAFT equation for the polymer–supercritical solvent systems is still limited since it is necessary to use a nonzero value for k_{ij}. As more systematic modeling studies are performed with polymer–supercritical solvent mixtures, it may be possible to provide general guidelines for estimating k_{ij} much in the same manner as is done with the Peng–Robinson equation for small molecule mixtures. The proposed methods used to calculate pure polymer parameters gives reasonable results in many cases, and it allows SAFT to be used for other than poly(ethylene) or poly(ethylene)-derived polymers. Further work is needed to extend the group contribution approach to other chemical families and to find a more accurate method to calculate the energy parameter of strongly polar polymers, for which it is not possible to use the value regressed for the monomer.

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