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# Vapor−Liquid Equilibrium in Diluted Polymer + Solvent Systems

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**ABSTRACT:** Vapor−liquid equilibrium data were determined for five polymer + methylbenzene systems under isothermal conditions between (333.15 and 373.15) K. The polymers studied include copolymers and terpolymers of octadecyl propenoate, propenoic acid, ethenylbenzene, and 1-vinyl-2-pyrrolidone because of their practical importance as flow improvers for crude oil and/or derivatives. An all-glass microebulliometer with circulation of the liquid phase was used for measurements of total pressure over polymer + methylbenzene mixtures. Two predictive group-contribution models (entropic−free volume and group contribution−Flory) were applied to estimate the phase behaviors of two polymer solutions; good agreement with the experimental data was achieved.

## INTRODUCTION

Flow-improver additives significantly improve the transport of crude oil, gas condensate, and derivatives. One such type of efficient additive includes copolymers and terpolymers synthesized by polymerization of octadecyl propenoate (ODP) with propenoic acid (PA), ethenylbenzene (EB), and 1-vinyl-2-pyrrolidone (VP). They have shown excellent results in separating paraffinic fractions and improving the pour point and rheological properties of crude oil samples from northern Croatia.[1,2]

Determining the physicochemical properties of pure polymeric additives and their mixtures over a whole composition range across a wide span of temperatures and pressures can show whether an additive is suitable for a specific application. Accurate thermodynamic data for polymer + solvent systems are the prerequisite for computer-aided synthesis, production process design, and its optimization. Group-contribution methods can tell a lot about the properties of pure polymers and polymer solutions and can be used to predict phase equilibria. Still, evaluation of particular group parameters is always based on experimental data. The demand for data on polymer + solvent systems has produced a number of experimental studies on vapor−liquid equilibria. Experimental techniques frequently exploited for the investigation of polymer solutions are summarized and discussed in ref 3.

In our earlier study,[4] we designed a new microebulliometer to quickly measure the total pressure of systems containing a solvent and a polymer or a nonvolatile component, for which only a small amount of material was at hand. The need to perform measurements on these systems has emerged because relevant phase equilibrium data are not available in the literature.

## EXPERIMENTAL EQUIPMENT AND PROCEDURE

The construction and testing of the new microebulliometer has been described elsewhere.[4] The whole experimental setup consists of two big buffer volumes interconnected with a quartz digital manostat (Ruska Instruments Corp., Houston, TX), which is the usual configuration for determining vapor−liquid equilibrium. Temperature was measured using a calibrated digital thermometer (model F-250, Automatic Systems Laboratories, Redhill, U.K.) with an uncertainty of 0.01 K. Pressure in the system was determined indirectly from the boiling point of water in a parallel reference ebulliometer; the uncertainty was 0.02 kPa. It is assumed that vapor phase contains solvent only. Detailed testing and discussion concerning the error due to a small holdup of solvent in the vapor-phase part of the still was published in the previous paper.[4] It was proved that for similar types of systems, the absolute error in the pressure is less than 0.1 kPa within the same concentration region. Moreover, the error in the activity value is minimized because of the fact that partial pressure of the solution is related to the experimental pressure of the pure solvent, which is determined using the same procedure. The error in the experimental activity is dependent on pressure. For the highest experimental pressure (74 kPa), the relative uncertainty in pressure (i.e., ± 0.02 kPa) yields an uncertainty in the activity equal to ± 0.0003; for the lowest pressure (18 kPa), this uncertainty is equal to ± 0.0010. Therefore, the mean activity uncertainty is estimated as ± 0.0005 for all of the data presented.

To determine the total pressure of a solution, liquid mixtures were prepared directly in the microebulliometer by weighing both the solvent and the polymer; the typical volume of a liquid sample was about 7 cm$^3$. Next, the boiler was adjusted to smooth boiling, and the desired temperature was attained by adjusting the pressure in the system with a digital manostat. As the mixture volume was small, the equilibrium pressure was reached within several minutes, as indicated by the constant boiling point of water in the reference ebulliometer. As soon as the measurement of a mixture was completed, an additional amount of polymer was added to the equilibrium still to increase the polymer concentration in the system. Accidental loss of solvent during

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**Table 1. Chemical Composition, Number-Average Molar Mass $M_n$, and Weight-Average Molar Mass $M_w$ of Co- and Terpolymers**

| polymer | $M_n$/g·mol$^{-1}$ | $M_w$/g·mol$^{-1}$ |
|---|---|---|
| poly(ODP$_{0.85}$−EB$_{0.15}$) | 20700 | 31000 |
| poly(ODP$_{0.95}$−PA$_{0.05}$) | 10000 | 18500 |
| poly(ODP$_{0.82}$−EB$_{0.05}$−PA$_{0.13}$) | 15700 | 32100 |
| poly(ODP$_{0.82}$−EB$_{0.04}$−PA$_{0.14}$) | 22100 | 40200 |
| poly(ODP$_{0.79}$−EB$_{0.05}$−PA$_{0.16}$) | 14200 | 28600 |
| poly(ODP$_{0.79}$−PA$_{0.11}$−VP$_{0.10}$) | 15900 | 36300 |
| poly(ODP$_{0.78}$−EB$_{0.05}$−VP$_{0.17}$) | 19700 | 36600 |

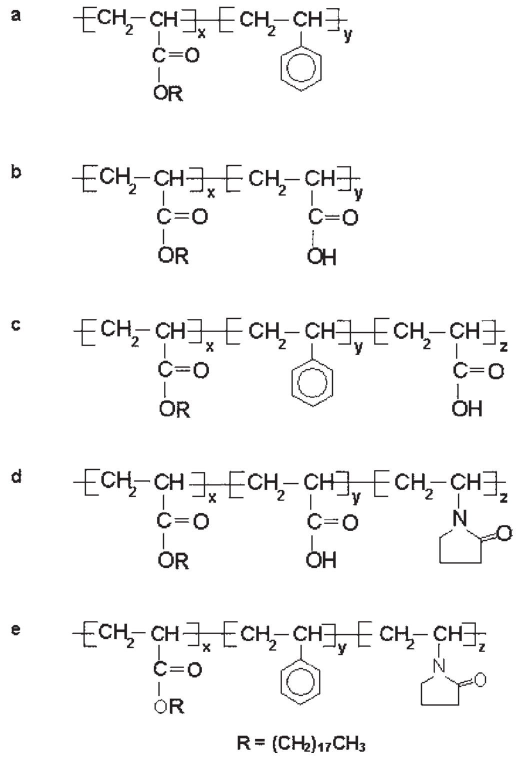

**Figure 1.** Structural formulas of (a) copolymer ODP−EB, (b) copolymer ODP−PA, (c) terpolymer ODP−EB−PA, (d) terpolymer ODP−PA−VP, and (e) terpolymer ODP−EB−VP.

opening of the apparatus could be neglected because each addition to the still was realized after the still was cooled to room temperature and took only a few seconds. Since the overall composition of the charged sample was determined gravimetrically, the error in the composition could be estimated as ± 0.0001 in the mass fraction, *w*.

## PREPARATION OF POLYMERS

Polymeric additives (i.e., copolymers and terpolymers) were prepared by free-radical solution polymerization of ODP with EB, PA, and VP in dimethylbenzene using Trigonox 21C70 as the initiator, as described previously.[2] Polymerization was performed in a reaction flask equipped with a condenser, mechanical stirrer, and temperature controller. The reaction took place in nitrogen atmosphere at 365 K for 5 h with continuous stirring. During that time, more than 95 % of the monomer was polymerized. The resulting homogeneous product was then cooled to room temperature. The ultimate polymer was isolated from the reaction mixture by repeated dissolution in methylbenzene and precipitation with methanol. This ensured complete removal of unreacted monomer. The polymer was finally dried under vacuum at 333 K. The $^1$H NMR spectrum confirmed the absence of unreacted monomer in the synthesized polymers. The chemical compositions and molar masses of the co- and terpolymers are summarized in Table 1, and their structures are shown in Figure 1.

## TOTAL PRESSURE MEASUREMENT

Five structurally different additives, namely, poly(ODP$_{0.85}$−EB$_{0.15}$), poly(ODP$_{0.95}$−PA$_{0.05}$), poly(ODP$_{0.82}$−EB$_{0.05}$−PA$_{0.13}$), poly(ODP$_{0.79}$−PA$_{0.11}$−VP$_{0.10}$), and poly(ODP$_{0.78}$−EB$_{0.05}$−VP$_{0.17}$), were selected for use in measurements of the total pressure over mixtures with methylbenzene. Subscripts denote the mole fractions of monomers in the copolymer or terpolymer. Vapor pressure measurements carried out at five equidistant isotherms within the range from (333.15 to 373.15) K are summarized in Table 2; they are expressed in terms of the methylbenzene activity $a_1 = P_1/P_1°$, where $P_1$ is the partial pressure and $P_1°$ is the vapor pressure of pure methylbenzene. Only two mixtures for each system were measured because of the small amounts of the polymers available.

**Table 2. Experimental Saturated Vapor Pressures $P_1°$ of Methylbenzene, Partial Pressures $P_1$ of the Methylbenzene (1) + Polymer (2) Systems, and Evaluated Activities $a_1 = P_1/P_1°$ as Functions of Temperature $T$ and Mass Fraction $w_1$**

| | | poly(ODP$_{0.85}$−EB$_{0.15}$) | | | poly(ODP$_{0.95}$−PA$_{0.05}$) | | | poly(ODP$_{0.82}$−EB$_{0.05}$−PA$_{0.13}$) | | | poly(ODP$_{0.79}$−PA$_{0.11}$−VP$_{0.10}$) | | | poly(ODP$_{0.78}$−EB$_{0.05}$−VP$_{0.17}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $T$/K | $P_1°$/kPa | $w_1$ | $P_1$/kPa | $a_1$ | $w_1$ | $P_1$/kPa | $a_1$ | $w_1$ | $P_1$/kPa | $a_1$ | $w_1$ | $P_1$/kPa | $a_1$ | $w_1$ | $P_1$/kPa | $a_1$ |
| 333.15 | 18.57 | 0.9561 | 18.43 | 0.9925 | 0.9211 | 18.46 | 0.9941 | 0.8896 | 18.46 | 0.9941 | 0.8829 | 18.19 | 0.9795 | 0.9427 | 18.54 | 0.9984 |
| 333.15 | 18.57 | 0.9796 | 18.53 | 0.9978 | 0.9615 | 18.54 | 0.9984 | 0.9440 | 18.52 | 0.9973 | 0.9387 | 18.49 | 0.9957 | 0.9760 | 18.56 | 0.9997 |
| 343.15 | 27.23 | 0.9561 | 27.05 | 0.9934 | 0.9211 | 27.01 | 0.9919 | 0.8896 | 27.06 | 0.9938 | 0.8829 | 26.70 | 0.9805 | 0.9427 | 27.19 | 0.9985 |
| 343.15 | 27.23 | 0.9796 | 27.18 | 0.9982 | 0.9615 | 27.19 | 0.9985 | 0.9440 | 27.15 | 0.9971 | 0.9387 | 27.11 | 0.9956 | 0.9760 | 27.22 | 0.9996 |
| 353.15 | 38.93 | 0.9561 | 38.79 | 0.9964 | 0.9211 | 38.63 | 0.9923 | 0.8896 | 38.46 | 0.9879 | 0.8829 | 38.31 | 0.9841 | 0.9427 | 38.87 | 0.9985 |
| 353.15 | 38.93 | 0.9796 | 38.88 | 0.9987 | 0.9615 | 38.87 | 0.9985 | 0.9440 | 38.81 | 0.9969 | 0.9387 | 38.77 | 0.9959 | 0.9760 | 38.92 | 0.9997 |
| 363.15 | 54.38 | 0.9561 | 54.24 | 0.9974 | 0.9211 | 53.86 | 0.9904 | 0.8896 | 53.59 | 0.9855 | 0.8829 | 53.65 | 0.9866 | 0.9427 | 54.27 | 0.9980 |
| 363.15 | 54.38 | 0.9796 | 54.32 | 0.9989 | 0.9615 | 54.31 | 0.9987 | 0.9440 | 54.19 | 0.9965 | 0.9387 | 54.13 | 0.9954 | 0.9760 | 54.36 | 0.9996 |
| 373.15 | 74.40 | 0.9561 | 74.10 | 0.9960 | 0.9211 | 73.62 | 0.9895 | 0.8896 | 73.43 | 0.9870 | 0.8829 | 73.44 | 0.9871 | 0.9427 | 74.24 | 0.9978 |
| 373.15 | 74.40 | 0.9796 | 74.27 | 0.9983 | 0.9615 | 74.33 | 0.9991 | 0.9440 | 74.14 | 0.9965 | 0.9387 | 74.05 | 0.9953 | 0.9760 | 74.37 | 0.9996 |

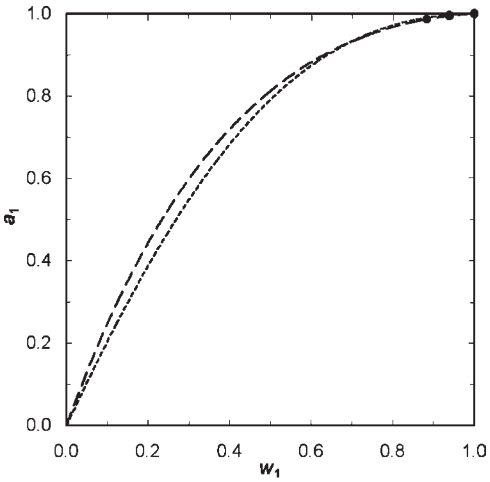

**Figure 2.** Activity $a_1$ of methylbenzene in poly(ODP$_{0.79}$−PA$_{0.11}$−VP$_{0.10}$) [$M_n$ = 15900 g·mol$^{-1}$; $M_w$ = 36300 g·mol$^{-1}$] as a function of methylbenzene mass fraction $w_1$ at 363.15 K: •, experimental data; ····, prediction of the entropic−FV model; — — —, prediction of the GC−Florymodel.

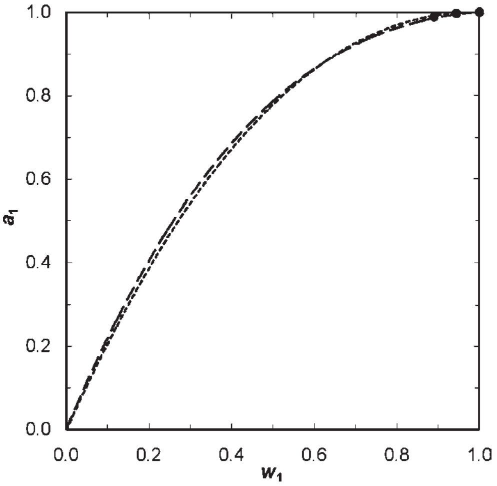

**Figure 3.** Activity $a_1$ of methylbenzene in poly(ODP$_{0.82}$−EB$_{0.05}$−PA$_{0.13}$) [$M_n$ = 15700 g·mol$^{-1}$; $M_w$ = 32100 g·mol$^{-1}$] as a function of methylbenzene mass fraction $w_1$ at 353.15 K: •, experimental data; ····, prediction of the entropic−FV model; — — —, prediction of the GC−Flory model.

## RESULTS AND DISCUSSION

To analyze the obtained data, we opted for the prediction of phase behavior, as the data of two experimental points, including concentration end points, could not be reduced with use of the *uni*versal *qua*si*c*hemical (UNIQUAC) equation, as was done, for example, in the Polymer Solution Data Collection by Hao et al.[3]

We used two predictive models, the entropic−free volume (entropic−FV) activity coefficient model[5] and the group contribution−Flory equation of state (GC−Flory EOS) model,[6] to estimate the activities of methylbenzene in mixtures with a polymer. Both models are based on the group-contribution method. The first exploits the activity coefficient approach, which requires accurate volume data for both the solvent and the polymer at the temperature of the system. The second was originally developed as an equation of state; no volumes of pure components and mixtures are required. The necessary equations, calculation procedure, and parameters are available in Kontogeorgis et al.[5] for the entropic−FV model and in Bogdanić and Fredenslund[6] for the GC−Flory model.

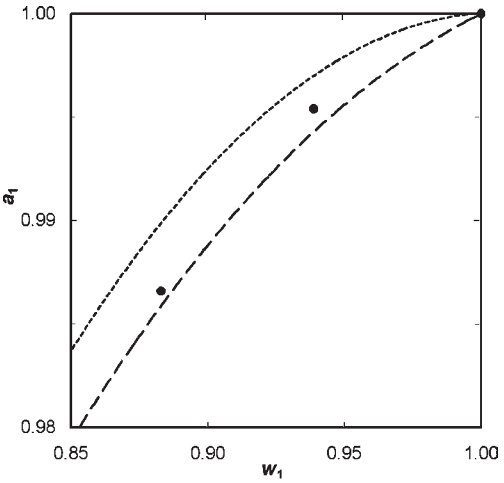

**Figure 4.** Activity $a_1$ of methylbenzene in poly(ODP$_{0.79}$−PA$_{0.11}$−VP$_{0.10}$) [$M_n$ = 15900 g·mol$^{-1}$; $M_w$ = 36300 g·mol$^{-1}$] as a function of methylbenzene mass fraction $w_1$ at 363.15 K (enlarged region in the vicinity of the pure solvent): •, experimental data; ····, prediction of the entropic−FV model; — — —, prediction of the GC−Flory model.

The first step is to divide the structure of polymeric compounds into groups defined by the model. In the entropic−FV model, the required parameters are the group areas and volumes calculated by Bondi.[7] Group interaction parameters for all possible binary pairs of groups can be found in the table of temperature-dependent *uni*versal *f*unctional *a*ctivity *c*oefficient (UNIFAC) parameters.[8] The procedure also requires knowledge of pure-component densities and molar masses. The average molar mass of the polymer should be used whenever possible. The parameters needed for the GC−Flory model are the group areas and volumes derived by Bondi,[7] the EOS parameters defined in terms of corresponding group parameters, the interaction energies between like and unlike groups, and the molar masses of all components.

Two terpolymers, namely, poly(ODP$_{0.79}$−PA$_{0.11}$−VP$_{0.10}$) and poly(ODP$_{0.82}$−EB$_{0.05}$−PA$_{0.13}$), in mixtures with methylbenzene were chosen as examples of solvent activity predictions because values for all of the necessary group parameters for both models were at hand. The densities of the polymers required by the entropic−FV model were calculated using the simple group contribution−*vol*ume (GCVOL) model,[9] as described earlier by Bogdanić and Fredenslund.[10]

Figures 2 and 3 show the prediction of methylbenzene activities in poly(ODP$_{0.79}$−PA$_{0.11}$−VP$_{0.10}$) and poly(ODP$_{0.82}$−EB$_{0.05}$−PA$_{0.13}$), respectively. It is obvious that the models are mutually comparable and in good agreement. The enlarged areas in the vicinity of the pure solvent from Figures 2 and 3 are shown in Figures 4 and 5, respectively; they illustrate the reliability of the two predictive methods. Moreover, the dependence of the solvent activity on concentration provides a qualitative description of a particular system's behavior over the whole concentration range, including activity trends, since the prediction is based on group contributions, which represent the structures of the components involved. This is a way to avoid purely empirical background. It is necessary to point out that prediction

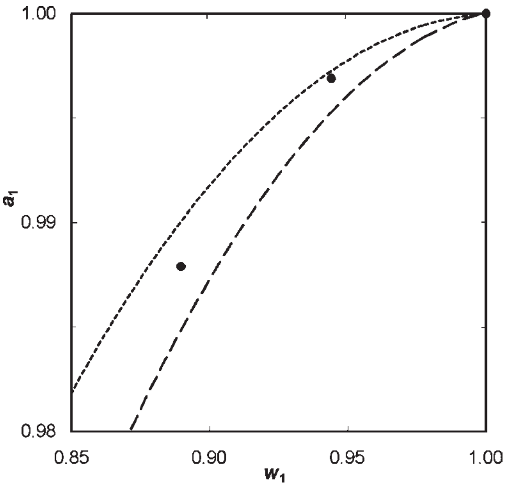

**Figure 5.** Activity $a_1$ of methylbenzene in poly(ODP$_{0.82}$−EB$_{0.05}$−PA$_{0.13}$) [$M_n$ = 15700 g·mol$^{-1}$; $M_w$ = 32100 g·mol$^{-1}$] as a function of methylbenzene mass fraction $w_1$ at 353.15 K (enlarged region in the vicinity of the pure solvent): ●, experimental data; · · · ·, prediction of the entropic−FV model; — — —, prediction of the GC−Flory model.

procedures were used not for validation of the experimental data but rather to give an idea about the trend in activity as a function of concentration. Although mixtures in the concentration region of the pure solvent could exhibit ideal behavior, the magnitude of the slope of the activity-versus-concentration curve at infinite dilution largely influences the shape of the predictive curve, which could be rather different for different systems.

## ■ CONCLUSIONS

The total pressures over five polymer + methylbenzene systems have been experimentally determined in diluted concentrations of polymer and expressed in terms of activity. The measured data have been compared with values predicted by two group-contribution models, namely, the entropic−FV and GC−Flory models. The agreement between the experimental and predicted values has confirmed the good performance of both the experimental procedure and the estimation methods.

## ■ AUTHOR INFORMATION

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## ■ REFERENCES

(1) Erceg Kuzmić, A.; Radošević, M.; Bogdanić, G.; Vuković, R. Flow improver additives for gas condensate. *Fuel* **2007**, *86*, 1409–1416.

(2) Erceg Kuzmić, A.; Radošević, M.; Bogdanić, G.; Srića, V.; Vuković, R. Studies on the influence of long chain acrylic esters polymers with polar monomers as crude oil flow improver additives. *Fuel* **2008**, *87*, 2943–2950.

(3) Hao, W.; Elbro, H. S.; Alessi, P. *Polymer Solution Data Collection. 1: Vapor−Liquid Equilibrium*; Chemistry Data Series, Vol. XVI, Part 1; DECHEMA: Frankfurt am Main, Germany, 1992.

(4) Pavlíček, J.; Bogdanić, G.; Wichterle, I. Circulation microebulliometer for determination of pressure above mixtures containing solvent and non-volatile component. *Fluid Phase Equilib.* **2010**, *297*, 142–148.

(5) Kontogeorgis, G. M.; Fredenslund, A.; Tassios, D. P. Simple activity coefficient model for the prediction of solvent activities in polymer solutions. *Ind. Eng. Chem. Res.* **1993**, *32*, 362–372.

(6) Bogdanić, G.; Fredenslund, A. Revision of the group-contribution Flory equation of state for phase equilibria calculations in mixtures with polymers. 1. Prediction of vapor−liquid equilibria for polymer solutions. *Ind. Eng. Chem. Res.* **1994**, *33*, 1331–1340.

(7) Bondi, A. *Physical Properties of Molecular Crystals, Liquids, and Glasses*; Wiley: New York, 1968.

(8) Hansen, H.; Coto, B.; Kuhlman, B. *UNIFAC with Linearly Temperature-Dependent Group Interaction Parameter*; SEP Publication; Engineering Research Center IVC-SEP, Technical University of Denmark: Lyngby, Denmark, 1992; No. 9212.

(9) Elbro, H. S.; Fredenslund, A.; Rasmussen, P. A new simple equation for the prediction of solvent activities in polymer solutions. *Macromolecules* **1990**, *23*, 4707–4714.

(10) Bogdanić, G.; Fredenslund, A. Prediction of vapor−liquid equilibria for mixtures with copolymers. *Ind. Eng. Chem. Res.* **1995**, *34*, 324–331.