Cosolvent Studies with the System Ethylene/Poly(ethylene-co-acrylic acid): Effects of Solvent, Density, Polarity, Hydrogen Bonding, and Copolymer Composition

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Dedicated to Prof. *André M. Braun* on the occasion of his 60th birthday

In the industrial high-pressure polymerization process, the manufacture of ethylene-based copolymers like poly(ethylene-co-acrylic acid) must be performed at very high pressures (up to 300 MPa) to avoid demixing due to unfavorable interactions between product (polymer) molecules and molecules of the educt mixture (ethylene and comonomer). Suitable inert cosolvents may help to lower the operating pressure and yet still operate in a single-phase region. In this paper, phase-equilibrium data are presented for mixtures of ethylene and ethylene-co-acrylic acid copolymer with and without the incorporation of various cosolvents in varying amounts. It was found that nonpolar but dense cosolvents like heptane, 2,2,4-trimethylpentane, and decane match the cosolvent potential of a polar but nonassociating substance like AcOEt, especially at the higher temperatures investigated. Strongly polar and associating fluids like EtOH and octanoic acid are superior cosolvents. However, for high concentrations of EtOH and lower temperatures, a shift in phase behavior with increasing demixing pressures has been observed and is attributed to self-association of excess EtOH molecules. This phenomenon is not observed for AcOEt and octanoic acid.

1. Introduction. – In several industrial processes dealing with the production and processing of ethylene-based copolymers, it is of vital importance to operate in a single-phase region, for instance, to avoid overheating due to fouling problems. However, due to unfavorable low-strength interactions between the mixing partners compared to likewise interaction, such processes usually have to be carried out at very high pressures, up to 300 MPa [1].

This situation is strongly exacerbated by the random incorporation of polar comonomers in the backbone of the polyethylene chain. Under the operating conditions to be found in the high-pressure-polymerization reactor, typically with mixtures of ethylene/comonomer/copolymer, due to increased polymer-polymer interactions, the phase boundary is shifted to higher pressures when the comonomer used is not capable of acting as a cosolvent or when its concentration is very low. Here, the comonomer concentration is subject to the desired product characteristic and can not be altered independently in order to depress the process pressure applied.

Thus, it is economically and technically desirable to lower the pressures required by the addition of inert cosolvents capable both of establishing polar interactions with the comonomer in the polymer chain and raising the overall density of the solvent mixture. The fundamentals of the phase behavior of strongly asymmetric mixtures like the ones treated in this paper have been discussed elsewhere [2].

In this work, phase-equilibria data (cloud points) are presented for (quasi)binary and (quasi)ternary mixtures of ethylene/ethylene-co-acrylic acid copolymer (EAA) and ethylene/cosolvent/ethylene-co-acrylic acid copolymer, respectively.

Acrylic acid (AA) repeat units tend to establish intramolecular and likewise intermolecular H-bonds (dimerization), thus shifting the pressures required for the occurrence of a single phase to higher values even when the AA content in the polymer backbone is relatively low (see *Fig. 1*). As cosolvent model substances for lowering the demixing pressure, we have chosen AcOEt as a polar cosolvent and EtOH and octanoic acid (OA) as both polar and associating cosolvents. To decouple cosolvency effects attributed merely to the increase in density triggered by the incorporation of a liquid cosolvent from those deriving from the cosolvent's ability to establish favorable interactions with the repeat units in the polymer chain, the following nonpolar substances with comparable molecule size and *P-V-T* behavior have been employed as well: heptane, 2,2,4-trimethylpentane, and decane.

2. Experimental. – 2.1. *Method.* A static-high-pressure view cell with a magnetic stirring device was used to obtain cloud points. Details of the exper. setup were described by *Müller* [3]. The cell is equipped with a steel bellows to vary volume (pressure) and a sapphire window along with an optical system (light source, borescope, camera, and monitor) for visual observation of the system.

For all experiments, the polymer (5% of the desired overall mass of the mixture) is filled into the cell. The cell is assembled and inserted into the apparatus. Then, the cell is evacuated to approx. $2 \cdot 10^{-3}$ mbar and subsequently purged with ethylene several times to remove any entrapped air. When cosolvent has to be added, the cosolvent is injected into the cell with a syringe through one of the cell's ports against counterflowing ethylene to avoid importing O_2. The cell is sealed and pressurized with ethylene until the desired pressure is reached. Then, the mixture is stirred and heated to 200–250°.

After homogenization of the system, cloud points (demixing pressures) can be determined isothermically. The system pressure is set well above the expected demixing pressure. Then, the pressure is lowered slowly. Upon reaching the cloud point, the demixing system becomes so opaque that it is no longer possible to see the stir bar. This is our definition of the cloud point.

2.2. *Materials.* The polymers examined in this study were pure low-density polyethylene (LDPE) and ethylene-based random copolymers with 6, 7.5, 8, 9, 11 and 15% AA content (EAA_6, $EAA_{7.5}$, EAA_8, EAA_9, EAA_{11}, EAA_{15}) in the polymer backbone, respectively. Of these, only the copolymers EAA_6, $EAA_{7.5}$ and EAA_9 were employed for the cosolvent studies. Physical data for the polymers are listed in *Table 1*. The EAA-copolymers were kindly donated by *Exxon Co.*, the LDPE was donated by *BASF AG.*

On all polymer samples, gel-permeation chromatography (GPC) was performed with LDPE standards. AA Repeat units were converted to ester units first to avoid interaction with the GPC column. All cosolvents were

Table 1. *Physical Data for the Polymers Used in the Study*[a])

Polymer	AA content [%]	AA content [mol-%]	M_n [g/mol]	M_w [g/mol]	M_w/M_n
LDPE	0	0	19235	164664	8.6
EAA_6	6.0	2.4	22713	258214	11.4
$EAA_{7.5}$	7.5	3.1	19932	235146	11.8
EAA_8	8.0	3.5	–	–	–
EAA_9	9.0	3.7	23443	227427	9.7
EAA_{11}	11.0	4.6	23730	205024	8.6
EAA_{15}	15.0	6.4	–	–	–

[a]) M_n is the number-average molecular mass, M_w the weight-average molecular mass, and M_w/M_n is the polydispersity.

Table 2. *Physical Data for the Monomers and (Co)solvents Studied*[a])

Monomer, (co)solvent	T_c [°]	p_c [bar]	M [g/mol]	ρ_l [g/cm^3]	μ [D]	$\boldsymbol{Q}$ [10^{40} C m^2]
Ethylene	282.4	50.4	28.05	0.58 (163 K)	0	5.0
AA	615	56.7	72.06	1.05	≈1.5	–
AcOEt	523.2	38.3	88.11	0.90	1.9	–
EtOH	513.9	61.4	46.07	0.79	1.7	–
OA	421.9	26.4	144.21	0.91	–	–
Heptane	267.2	27.4	100.21	0.68 (15°)	0	–
2,2,4-Trimethylpentane	304.1	25.7	114.23	0.69	–	–
Decane	344.5	21.1	142.29	0.73	0	–

[a]) Subscript *c* denotes critical data, ρ_l is the liquid density, μ and $\boldsymbol{Q}$ are dipole and quadrupole moments, respectively. Data taken from [4]. The approximate dipole moment value of AA was taken from [7].

purchased and used as received. Physical data for the cosolvents were taken from literature and are listed in *Table 2* [4]. Ethylene (purity 3.4) was donated by *BASF AG* and was used as received.

3. Results and Discussion. – In *Fig. 1*, demixing (cloud point) curves for binary mixtures of 5% polymer in ethylene (*Table 3*) are presented. Compared to the results for pure polyethylene, the demixing pressures are shifted to much higher values when AA repeat units are present in the backbone of the polymer.

For the polymer containing only 6% AA at 150°, the cloud point is shifted up by *ca.* 600 bar. For EAA$_{11}$, a shift of this magnitude takes place already at 200°. The

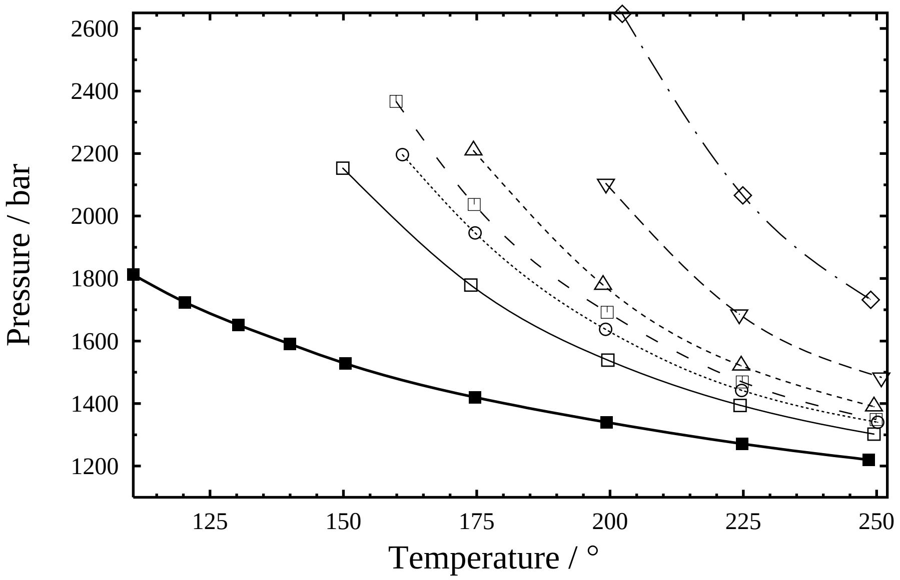

Fig. 1. *Cloud-point curves for quasibinary systems of ethylene and EAA copolymers.* The AA mass fraction percentage of polymer mass is given as subscript; the polymer concentration is fixed at 5%: (■) LDPE, (□) EAA$_6$, (○) EAA$_{7.5}$, (⊡) EAA$_8$, (△) EAA$_9$, (▽) EAA$_{11}$, (◇) EAA$_{15}$.

Table 3. *Experimental Cloud-Point Data* (demixing pressures) *Obtained for the Quasibinary Systems Investigated*[a]). Data are given in order of descending temperature for better comparability.

LDPE		EAA_6		$EAA_{7.5}$		EAA_8	
T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]
248.5	1221	249.5	1302	250.2	1340	249.9	1349
224.8	1272	224.4	1394	224.7	1442	224.8	1469
199.4	1341	199.6	1539	199.2	1637	199.5	1692
174.7	1421	173.9	1779	174.7	1946	174.5	2037
–	–	–	–	161.1	2196	159.9	2367
150.4	1529	149.9	2153	–	–	–	–
140.0	1591	–	–	–	–	–	–
130.3	1653	–	–	–	–	–	–
120.3	1725	–	–	–	–	–	–
110.6	1813	–	–	–	–	–	–

EAA_9		EAA_{11}		EAA_{15}	
T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]
249.5	1390	250.9	1484	248.9	1732
224.6	1521	224.2	1686	224.9	2066
198.7	1779	199.2	2104	202.3	2647
174.4	2209	–	–	–	–

[a]) Quasibinary systems: ethylene/polymer, $w_{\text{Ethylene}} = 0.95$, $w_{\text{Polymer}} = 0.05$, where w is the mass fraction.

intermolecular forces accounting for this type of phase behavior vary as a function of $1/T$. This explains the high sensitivity of the demixing pressures in the lower-temperature region [5]. Results for quasibinary systems containing ethylene and AA copolymers have, for instance, been published by *Luft* and *Wind* [6] and *McHugh* and co-workers [7][8]. *Fig. 2* shows a comparison of our data for a polymer fraction of 5.0% to data of *Luft* and *Wind* [6] for a copolymer also containing 6% AA (M_w = 150 kg/mol) and also produced by the same manufacturer with a polymer fraction of 3.8% resp. 5.7% in the mixture. As expected, the data for 5.0% of polymer contents is embedded in the data taken from literature. Even though the polymer content differs, it can be concluded that the literature data could be reproduced well. Good agreement with the data of *McHugh* and co-workers was found, too, but a comparative plot is not shown here because EAA copolymers each with slightly differing AA content were investigated in those publications.

In *Fig. 3*, the impact of the addition of a small amount of cosolvent on the phase behavior is shown. For these experiments, 5% of the cosolvents were added to the mixture of ethylene and EAA_6 (*Table 4*). It can be seen that similar results with only slight depression of the cloud-point curve were obtained for the three nonpolar cosolvents and the polar substance AcOEt.

For the nonpolar cosolvents, the cloud-point pressure could be depressed by 45–150 bar over the whole temperature range. Compared to the other two substances, 2,2,4-trimethylpentane at lower temperatures shows slightly better cosolvent behavior. While acting very similarly at higher temperatures, the AcOEt can act as a better cosolvent at lower temperatures due to its polar nature.

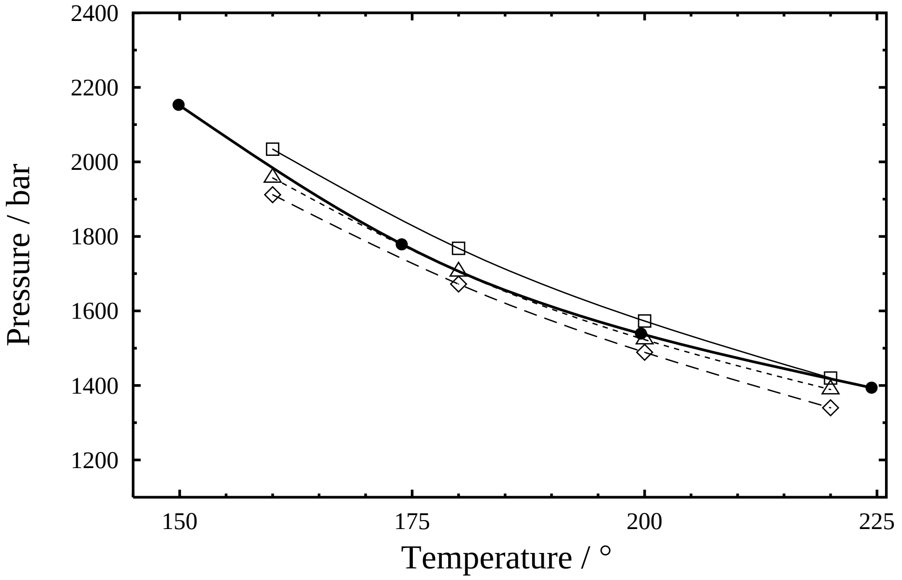

Fig. 2. *Cloud-point curves for quasibinary systems of ethylene/EAA$_6$.* The mass fraction of polymer w_{Polymer} = (●) 0.050. Comparison with *Wind*'s data [6b]; w_{Polymer} = (□) 0.038, (△) 0.057, (◇) 0.076.

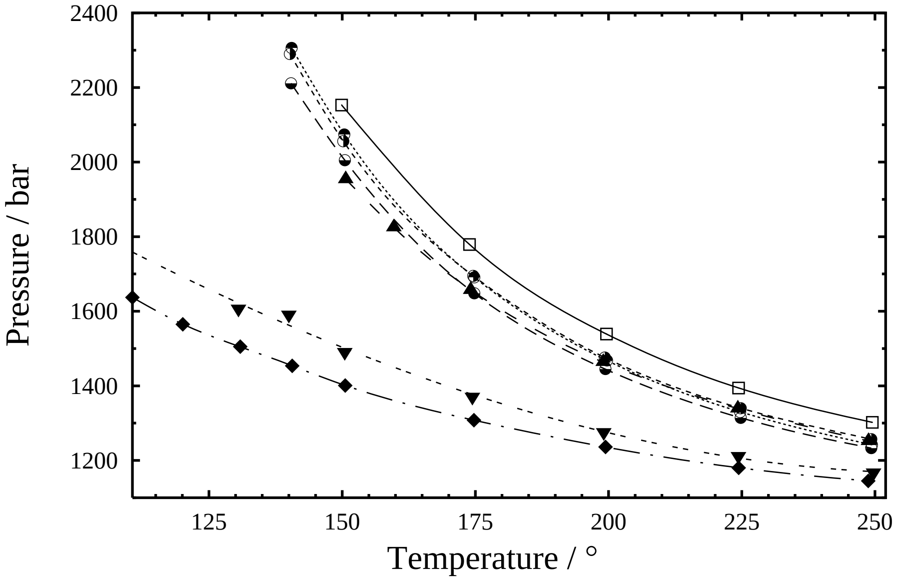

Fig. 3. *Cloud-point curves for quasiternary systems of ethylene/*ca. *5% cosolvent/EAA$_6$.* The polymer concentration is fixed at 5%; w is the cosolvent mass fraction in the system: (□) $w = 0$; (◓) w_{Decane}, (◑) w_{Heptane}, (◒) $w_{\text{2,2,4-Trimethylpentane}}$, (▼) $w_{\text{EtOH}} = 0.050$; (▲) $w_{\text{AcOEt}} = 0.055$; (◆) $w_{\text{OA}} = 0.046$.

Table 4. *Experimental Cloud-Point Data* (demixing pressures) *Obtained for the Quasiternary Systems Investigated*[a])

$w_{\mathrm{Heptane}} = 0.050$		$w_{\mathrm{Heptane}} = 0.398$		$w_{\mathrm{2,2,4\text{-}Trimethylpentane}} = 0.050$		$w_{\mathrm{2,2,4\text{-}Trimethylpentane}} = 0.399$	
T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]
249.3	1257	249.7	863	249.3	1233	249.8	888
224.8	1340	224.9	910	224.8	1314	224.9	944
199.3	1476	199.9	993	199.4	1445	199.1	1036
174.6	1695	175.2	1129	174.8	1648	174.8	1181
150.2	2056	150.6	1366	150.5	2005	150.6	1430
140.2	2290	140.6	1515	140.4	2211	140.1	1586
–	–	130.3	1709	–	–	130.4	1784
–	–	120.5	1961	–	–	–	–

$w_{\mathrm{Decane}} = 0.050$		$w_{\mathrm{Decane}} = 0.402$		$w_{\mathrm{AcOEt}} = 0.055$		$w_{\mathrm{AcOEt}} = 0.398$	
T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]
249.4	1242	249.5	799	248.8	1252	250.1	936
224.7	1330	225.2	844	224.3	1339	225.0	974
199.7	1468	200.0	917	199.0	1464	199.7	1019
174.8	1691	175.4	1041	174.1	1657	175.0	1099
–	–	–	–	159.7	1825	160.1	1168
150.4	2074	150.6	1260	150.7	1954	150.5	1224
140.5	2306	140.4	1406	–	–	140.9	1298
–	–	130.7	1581	–	–	130.0	1396
–	–	120.2	1818	–	–	–	–

$w_{\mathrm{AcOEt}} = 0.692$		$w_{\mathrm{EtOH}} = 0.050$		$w_{\mathrm{EtOH}} = 0.149$		$w_{\mathrm{EtOH}} = 0.247$	
T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]
249.8	666	249.7	1168	250.1	1036	250.0	966
225.2	677	224.4	1212	224.8	1074	224.9	981
200.0	701	199.1	1276	199.8	1119	199.5	1016
175.5	746	174.4	1371	175.0	1161	174.3	1069
150.6	842	150.5	1491	151.3	1271	150.0	1154
141.0	910	140.0	1591	141.0	1301	140.6	1209
130.5	1010	130.5	1607	131.0	1339	130.5	1264
120.6	1156	–	–	–	–	–	–

$w_{\mathrm{EtOH}} = 0.407$		$w_{\mathrm{OA}} = 0.046$		$w_{\mathrm{OA}} = 0.398$		$w_{\mathrm{OA}} = 0.658$	
T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]
248.7	811	248.7	1145	248.8	697	249.5	346
224.8	834	224.4	1180	224.9	691	224.8	325
199.9	886	199.4	1236	199.6	696	199.5	307
175.0	989	174.7	1308	174.6	706	175.5	289
150.4	1256	150.6	1401	150.5	719	150.9	269
140.9	1483	140.6	1454	141.0	728	141.1	260
–	–	130.9	1505	130.7	738	131.1	251
–	–	120.1	1565	120.5	749	120.4	243
–	–	110.6	1637	110.9	764	111.0	235

[a]) Quasiternary systems with ethylene, EAA_6 ($w_{\mathrm{Polymer}} = 0.05$), and a cosolvent.

A significantly different performance could be observed for both EtOH and OA. Especially at lower temperatures, both substances manage to lower the demixing pressure by several hundred bar: *e.g.*, for 150°, the addition of 5% OA to the system lowers the cloud-point pressure by more than 700 bar. Compared to EtOH, OA acts as the better cosolvent, which can be attributed to its carboxyl group and its higher molecular weight.

Fig. 4 shows the results obtained for the addition of 40% cosolvent. For such a high mass fraction of dense (compared to ethylene) cosolvent, all systems shown exhibit cloud points lowered by at least 360 bar over the whole temperature range. In this series, AcOEt is a less efficient cosolvent even than the nonpolar agents at higher temperatures (this may be attributed to its lower molecular weight). In the lower temperature region, this effect is reversed, showing AcOEt to be the superior cosolvent. Very powerful cosolvent behavior is demonstrated by OA over the entire temperature range. The cloud-point curve is virtually independent of temperature, the cloud-point pressure at 150°, for instance, is depressed by >1400 bar.

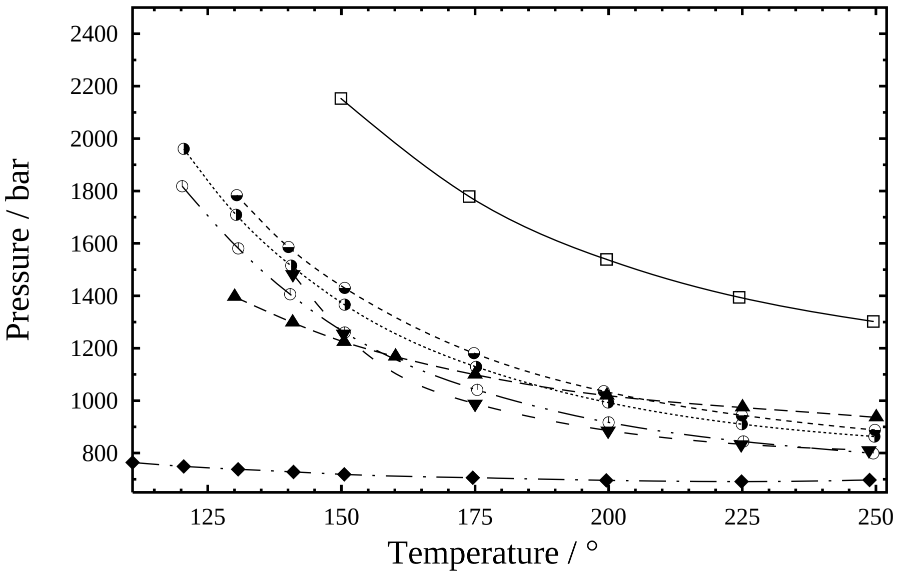

Fig. 4. *Cloud-point curves for quasiternary systems of ethylene/*ca. *40% cosolvent/EAA$_6$.* The polymer concentration is fixed at 5%; w is the cosolvent mass fraction in the system: (□) $w = 0$; (◑) $w_{\text{Heptane}} = 0.398$; (◒) $w_{2,2,4\text{-Trimethylpentane}} = 0.400$; (○) $w_{\text{Decane}} = 0.402$; (▲) $w_{\text{AcOEt}} = 0.398$; (▼) $w_{\text{EtOH}} = 0.407$; (◆) $w_{\text{OA}} = 0.398$.

However, quite different phase behavior was observed for EtOH. At higher temperatures, the cloud points are located *ca.* 100 bar below the points observed for addition of heptane or AcOEt. For temperatures below 175°, though, the cosolvent power seems to decrease dramatically. At 140°, the demixing pressures for EtOH and heptane addition become nearly equal and are located *ca.* 750 bar above the corresponding value for OA. This phase behavior can be attributed to strong self-association between EtOH molecules due to their excess concentration compared to the number of AA sites available in the polymer backbone. Even though the occurrence of self-association for high concentrations of OA might be expected, too, we have not been able to observe this phenomenon for an OA mass fraction of up to 65%. Furthermore, as expected, no increase in cloud-point pressures could be observed for an addition of 70% AcOEt (see *Fig. 5*).

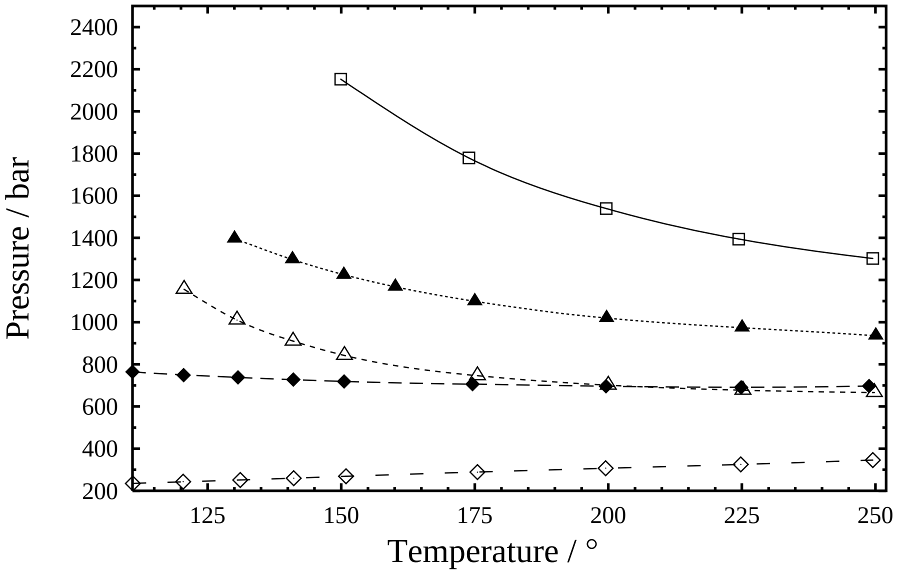

Fig. 5. *Cloud-point curves for quasiternary systems of ethylene/ca. 40–70% cosolvent/EAA_6.* The polymer concentration is fixed at 5%; *w* is the cosolvent mass fraction in the system: (□) $w = 0$; (▲) $w_{AcOEt} = 0.398$, (△) 0.692; w_{OA} = (◆) 0.398, (◇) 0.658.

To determine the concentration of EtOH for which the change in phase behavior takes place as precisely as possible, further experiments have been carried out for EtOH fractions of 15 and 25% (*Table 5* and *Fig. 6*). It can be seen that demixing pressures can be lowered substantially for a cosolvent addition up to about 15%. The step from 15–25% yields only a slight further pressure drop of *ca.* 100 bar over the entire temperature range. Further cosolvent addition (40%) at lower temperatures results in antisolvent behavior compared to the cloud-point curves observed for less EtOH. At 140°, the cloud point for 40% of EtOH is located only *ca.* 110 bar below the cloud point for 5%.

Our findings are consistent with the results published by *McHugh* and co-workers for the addition of EtOH to a system of butane and EAA-copolymer [9]. In that publication, a sharp rise in demixing pressure has been observed for adding 55.5% EtOH to a mixture of butane and 5% $EAA_{9.4}$ compared to adding 15.6% EtOH. *Wind* [6b] reports continuously decreasing cloud points when AA is added to systems of ethylene and 13.5% of EAA_3, EAA_6, or $EAA_{7.3}$, consistent with our results for adding OA to such systems. However, the highest AA content in the polymer examined by

Table 5. *Experimental Cloud-Point Data* (demixing pressures) *Obtained for the Quasiternary Systems Investigated*[a])

$EAA_{7.5}$				EAA_9			
$w_{EtOH} = 0.057$		$w_{EtOH} = 0.402$		$w_{EtOH} = 0.050$		$w_{EtOH} = 0.394$	
T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]	T [°]	p [bar]
250.2	1189	250.0	766	250.2	1200	250.9	795
224.6	1234	224.5	774	224.8	1243	225.0	804
199.4	1310	199.6	809	199.9	1331	199.5	826
174.8	1411	175.1	890	174.9	1439	174.8	873
–	–	160.1	989	–	–	–	–
150.6	1546	150.2	1079	150.7	1601	150.4	978
141.0	1604	–	–	140.7	1669	140.5	1051
130.7	1673	–	–	130.5	1746	130.5	1164
–	–	–	–	–	–	120.8	1334

[a]) Quasiternary systems with ethylene, EAA-copolymers ($w_{Polymer} = 0.05$), and EtOH as cosolvent.

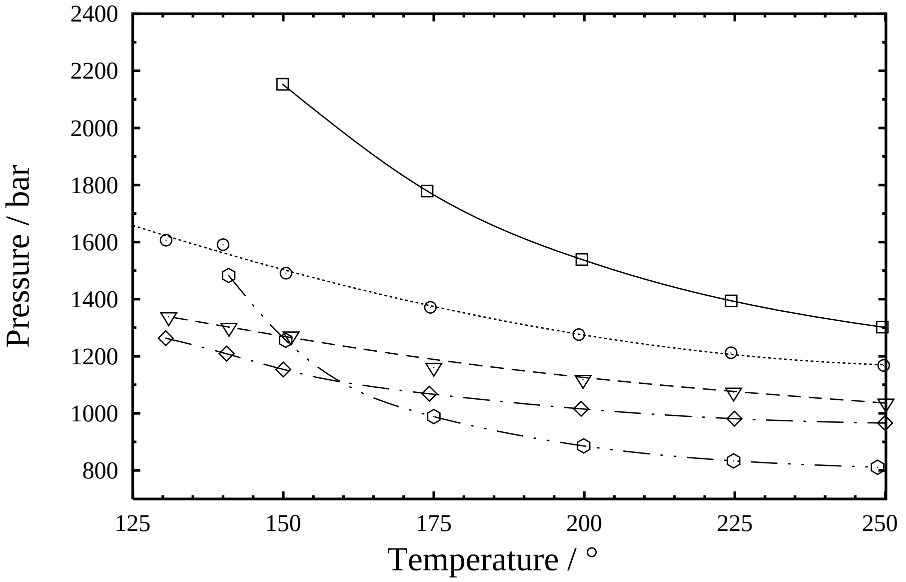

Fig. 6. *Cloud-point curves for quasiternary systems of ethylene/EtOH/EAA$_6$.* The polymer concentration is fixed at 5%; w_{EtOH} (the mass fraction of EtOH) = (□) 0, (○) 0.050, (▽) 0.149, (◇) 0.247, (⬡) 0.407.

Wind was 13.1%. To the best of our knowledge, no other data is available for ethylene/cosolvent/EEA systems to date.

In *Fig. 7*, the results obtained for the addition of EtOH to the system ethylene/EAA_6 (see *Fig. 6* as well) are compared to results for systems with $EAA_{7.5}$ and EAA_9, respectively. In the backbone of the latter two copolymers, more AA repeat units capable to establish interactions with the EtOH molecules are present. Thus, it is

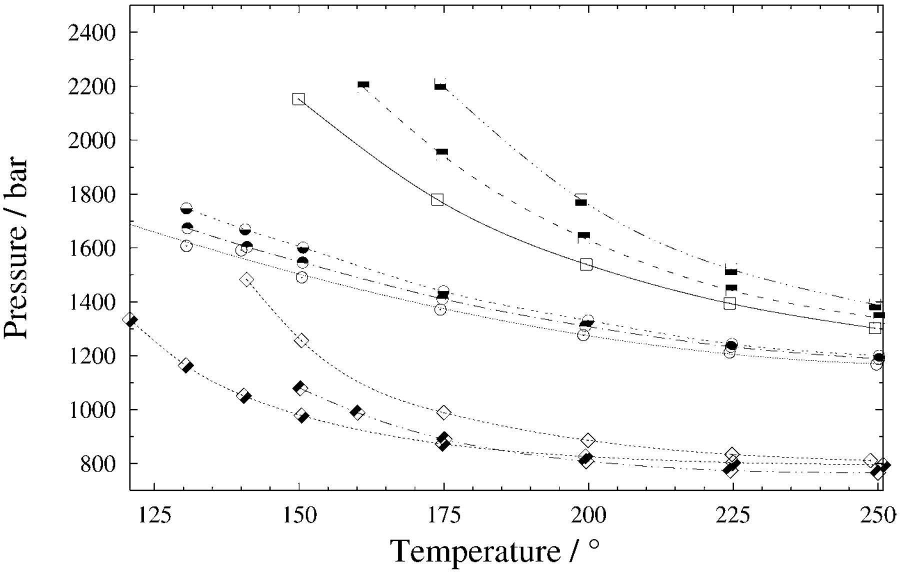

Fig. 7. *Cloud-point curves for quasiternary systems of ethylene/EtOH/EAA.* The mass fraction percentage of AA in the polymer (mass) is given as a subscript. The polymer concentration is fixed at 5%. EAA$_6$: w_{EtOH} = (□) 0, (○) 0.050, (◇) 0.407; EAA$_{7.5}$: w_{EtOH}=(⬒) 0, (◓) 0.057, (⬖) 0.402; EAA$_9$: w_{EtOH} = (⬓) 0, (◒) 0.050, (⬗) 0.394.

expected that fewer excess EtOH molecules remain unbound to consequently enter into self-association, which would lead to an increase in demixing pressure.

Without cosolvent addition, the phase behavior shown in *Fig. 1* observed with the EAA$_9$ system exhibits the highest demixing pressures. For 5% EtOH present in the mixture, very similar cloud-point values have been determined for the three polymer systems. It is remarkable that higher cloud-point pressures have been detected for the EAA$_{7.5}$ system compared with the EAA$_6$ system here. When adding small amounts of EtOH and differing AA contents in the polymer backbone, a competition takes place between the polymer's ability to saturate the EtOH and prevent self-association (favored by high AA contents) or to prevent strong polymer-polymer interactions (favored by low AA contents). When adding large amounts of EtOH (40%) to the former systems, the excess EtOH clearly is the determining factor for the resulting phase behavior. The EAA$_9$ system exhibits the lowest cloud-point data here. Strong EtOH self-association can take place in the EAA$_6$ system, shifting the demixing pressure up to the highest among the three polymer systems investigated.

Especially the three polar cosolvents investigated have strongly differing molecular masses, a situation that leads to rather different mole fractions in the mixtures compared to mass fractions. To further understand and assess the quite different cosolvent behavior observed, an isothermal plot for 150° is displayed in *Fig. 8*. For systems with ethylene, EAA$_6$, and polar cosolvents, the dependence of demixing pressure on the ratio of mole fractions of cosolvent and AA repeat units is shown (the ratio of mole fractions may be understood as the number of cosolvent molecules per AA repeat unit in the system). Note that EtOH molecules are assigned two associating

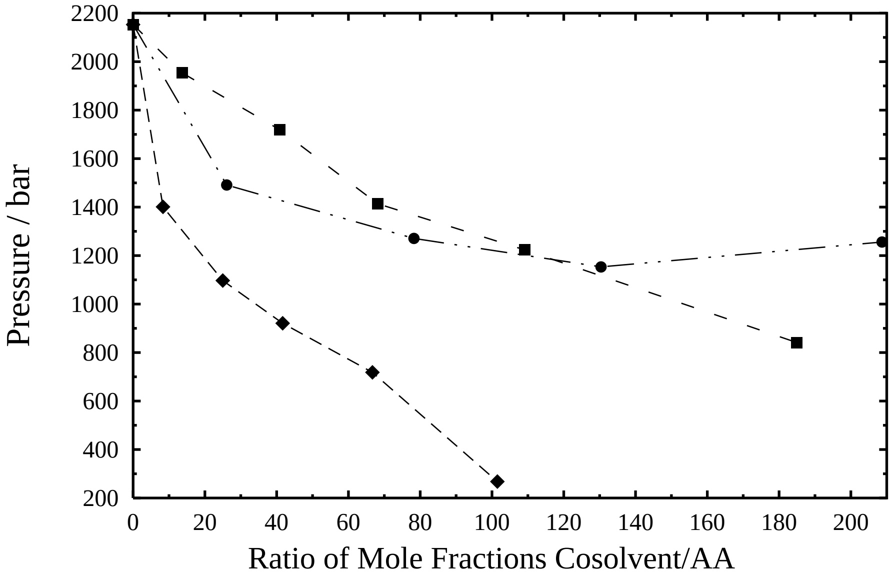

Fig. 8. *Isothermal* ($T = 150°$) *plot for the demixing-pressure dependence of the ratio of mole fractions cosolvent/AA*. $w_{\mathrm{Polymer}} = 0.050$; cosolvent = (■) AcOEt, (●) EtOH, (◆) OA.

sites compared to one site for a carboxylic acid molecule [10]. AcOEt merely acts as a proton acceptor and, thus, does not self-associate.

Once again, the outstanding power of the OA to lower the demixing pressure becomes evident. For low fractions, EtOH is the stronger cosolvent compared to AcOEt. This trend is reversed for higher fractions, though. Both AcOEt and EtOH show clearly inferior cosolvent capacity compared to OA. Saturation of the AA repeat units and subsequent elevation of demixing pressures due to cosolvent self-association occurs only in the range investigated when EtOH is used.

Owing to the comparatively low molecular mass of EtOH, the highest numbers of the ratio of mole fractions are attained. However, no indication of changing cosolvent behavior at higher mole-fraction ratios is observed for the other two substances.

4. Conclusions. – In mixtures of ethylene and poly(ethylene-co-acrylic acid) copolymers, nonpolar but dense cosolvents can perform equally well compared to the polar but nonassociating AcOEt.

For low temperatures with AcOEt or associating cosolvents over the entire temperature range under investigation, though, the depression of the cloud points measured is remarkably higher. However, at high concentrations and low temperatures, EtOH loses its cosolvent strength due to the occurrence of self-association.

Over the whole temperature range, OA acts as a very strong cosolvent in any concentration applied.

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