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The Mechanism of Phase Separation of Polymers in Organic Media—Apolar and Polar Systems

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Abstract

The phase separation properties of nine apolar and 15 polar systems, each comprising two polymers dissolved in one organic solvent, were examined in the light of recent developments in surface thermodynamics of polar components. A clear correlation existed between the sign of the total interfacial free energy of interaction of the system and the phase separation (or miscibility). Conversely, some of the phase separation results could be used to estimate the electron-donor surface tension parameters of methyl ethyl ketone and tetrahydrofuran.

INTRODUCTION

When two low molecular weight solutes are present in the same solution, i.e., with a common solvent, it is rare for the solution to break up spontaneously into two phases. However, when two solutions of different polymers in a common solvent are mixed, it is often found that two phases are formed, in organic (*1*) as well as in aqueous media (*2*).

Many studies have been done on phase separation of polymer solutions. According to Vrij (*3*), solutions of two different polymers in a common solvent will separate into two homogeneous phases when the entropy of mixing is small and there is a slight positive enthalpy of mixing, which gives rise to a positive Gibbs free energy of mixing. Most studies have been based on the determination of the enthalpy and entropy of mixing, using the Flory-Huggins formulation of the combinatorial entropy (*4*). Dobry and Boyer-Kawenoki (*1*) observed that some polymer pairs are compatible in some solvents but incompatible in others. Bank et al. (*5*) observed that polystyrene and poly(vinyl methyl ether) are compatible in toluene, benzene, or perchloroethylene, but incompatible in chloroform, methylene chloride, or trichorethylene. Thus, the solvent plays a crucial role in phase separation of polymer solutions. The incompatibility of polymers in a given solvent increases rapidly with an increase in molecular weight. From a thermodynamic point of view, if two dilute solutions of low molecular weight solutes in the same solvent are mixed, the system will form a single phase since the gain in entropy then usually outweighs the enthalpy of mixing. But if the solutions contain large molecules, the entropy of mixing becomes negligible. The solutions may then resist mixing and separate into two phases for any slightly positive enthalpy of mixing (*3*). The Flory-Huggins (*4*) approach to the determination of the thermodynamic properties of polymer solutions is usually considered applicable to the study of the compatibility or incompatibility of polymer systems. The Flory interaction parameters between each polymer and the solvent and between the two polymers are held to characterize intermolecular interactions completely.

In the final analysis, when the free energy of mixing (ΔG_{132}) of a system (comprising two Polymers 1 and 2 dissolved in a common Solvent 3) is negative, miscibility is favored, and when $\Delta G_{132} > 0$, incompatibility prevails, i.e., there will be phase separation. In *apolar* systems this approach has been successfully applied (*6*). Here a positive value for ΔG_{132} (or a negative value for the Hamaker constant A_{132} of the system) implies a repulsion between Polymers 1 and 2 dissolved in Solvent 3, and indeed, whenever $\Delta G_{132} > 0$, in *apolar* systems, separation occurs, and in *apolar* systems for which $\Delta G_{132} < 0$, miscibility is observed (*6*). The Flory-Huggins approach (*5*) applied to such apolar systems will yield the same correlation. However, recent studies on the interaction forces between *polar* materials have focused on certain unique attributes of these materials that place them outside the scope of the classical Flory-Huggins approach (*5*). Among these is the pronounced asymmetry in the complementarity, peculiar to polar (i.e., Lewis acid-base) interactions, which makes it possible for two different polar polymers to interact in much the same manner with a given polar solvent, while remaining capable of reacting very differently with each other, either through a strong mutual attraction (*7*) or by means of a strong repulsion (*8*), both for purely polar reasons. (The designation "polar" interactions, in this paper, pertains solely to electron acceptor-electron donor, or Lewis acid-base, interactions.) The role of polar repulsion is aqueous phase separation, and in partition, was discussed in an earlier paper (*8*). In this paper, phase separation of polymer pairs in both apolar and polar solvents is studied; aqueous systems (*8*) then are only an extreme example of the behavior in polar solvents.

THEORY

Some nine years ago a first attempt was made (*6*) to establish a correlation between the phase behavior of such polymer solutions and the sign of the Hamaker coefficient (*9*) that describes the three-component interaction in the system. In Ref. *6*, the Hamaker coefficient (A) was taken to be directly proportional to the free energy of cohesion $\Delta G_{ii}^{\mathrm{c}}$, according to

$$A_{ii} = -12\pi d_0^2 \Delta G_{ii}^{\mathrm{c}} \tag{1}$$

where

$$\Delta G_{ii}^{\mathrm{c}} = -2\gamma_i \tag{2}$$

and where d_0 is the minimum equilibrium distance between like molecules (*10*), and γ_i the surface tension of Substance i. The free energy of interaction of Substance i, e.g., a polymer, with Substance j, which may be a low-molecular weight liquid, is given in terms of the Hamaker coefficient by

$$A_{ij} = -12\pi d_{0ij}^2 \Delta G_{ij} \tag{3}$$

and

$$\Delta G_{ij} = \gamma_{ij} - \gamma_i - \gamma_j \tag{4}$$

For Polymers 1 and 2, dissolved in Solvent 3, the expressions employed (*6*) were

$$A_{132} = -12\pi d_0^2 \Delta G_{132} \tag{5}$$

and

$$\Delta G_{132} = \gamma_{12} - \gamma_{13} - \gamma_{23} \tag{6}$$

Equation (6) is the three-condensed phase analogue of the Dupré equation. A correlation was found (*6*) (which was valid for all but five of 31 pairs of polymers dissolved in various solvents) that if A_{132} was negative, as calculated by Eqs. (5) and (6), two phases were formed, one containing Polymer 1, the other containing Polymer 2. If A_{132} was positive, only one phase was formed.

In the light of more recent developments however, the concept of a single coefficient that would permit the characterization of both apolar and polar interactions with one factor appears to be a serious oversimplification. It has been demonstrated earlier, via the Lifshitz approach (*11–13*), that all three electrodynamic van der Waals interactions (London, as well as Debye and Keesom) should be treated in the same manner as they conform, on a macroscopic scale, to the same equation, of the type of Eq. (1). Thus, all three electrodynamic or Lifshitz-van der Waals (LW) interactions may, for convenience's sake, be grouped together under the application of apolar interactions.

Polar or electron donor–electron acceptor interactions, on the other hand, do not conform to the same equation as the combined apolar interactions. However, equations for electron acceptor–electron donor or Lewis acid-base (AB) interactions recently have been established, as have methods for the quantitative determination of the polar parameters of the interaction energy (*8*, *14–20*). It thus becomes feasible to reexamine most of the polymer phase separation and miscibility systems that were described earlier (*6*), in a more complete and rigorous manner. For the sake of clarity, apolar (LW) and polar (AB) systems will be treated separately. Results will in all cases be correlated with the sign of the total free energy of interaction, ΔG^{TOT}, as ΔG^{TOT} may be taken to be the sum of $\Delta G^{\mathrm{LW}} + \Delta G^{\mathrm{AB}}$ (*8*, *14–20*).

$$\Delta G^{\mathrm{TOT}} = \Delta G^{\mathrm{LW}} + \Delta G^{\mathrm{AB}} \tag{7}$$

This avoids the use of the Hamaker coefficient, which is only related to

ΔG^{LW} (Eq. 1), and not to ΔG^{AB}. When $\Delta G_{132}^{\mathrm{TOT}} < 0$, mixing should be favored, and when $\Delta G_{132}^{\mathrm{TOT}} > 0$, separation of two different Polymers 1 and 2 dissolved in an organic Solvent 3 should ensue.

I. Apolar Systems

The interaction between Polymers 1 and 2 dissolved in Solvent 3 is most aptly described by the analogue of the Dupré equation (Eq. 6). For strictly apolar (LW) systems the combining rule of Good and Girifalco (*21*) is valid:

$$\gamma_{ij}^{\mathrm{LW}} \equiv (\sqrt{\gamma_i^{\mathrm{LW}}} - \sqrt{\gamma_j^{\mathrm{LW}}})^2 \tag{8}$$

The sign and value of $\Delta G_{132}^{\mathrm{LW}}$ for any system can thus be determined in all cases where γ_1^{LW}, γ_2^{LW}, and γ_3^{LW} are known. For solids, $\gamma_{\mathrm{S}}^{\mathrm{LW}}$ can be determined by contact angle (θ) measurement with an apolar liquid of a known $\gamma_{\mathrm{L}}^{\mathrm{LW}}$, using Young's equation:

$$(1 + \cos\theta) = 2\sqrt{\gamma_{\mathrm{S}}^{\mathrm{LW}}/\gamma_{\mathrm{L}}^{\mathrm{LW}}} \tag{9}$$

For liquids, $\gamma_{\mathrm{L}}^{\mathrm{LW}}$ can be verified by means of contact angle determination on a known apolar solid (e.g., Teflon, with a $\gamma_{\mathrm{S}}^{\mathrm{LW}} \approx 18$ mJ/m^2), according to

$$(1 + \cos\theta)\gamma_{\mathrm{L}} = 2\sqrt{\gamma_{\mathrm{S}}^{\mathrm{LW}}\gamma_{\mathrm{L}}^{\mathrm{LW}}} \tag{10}$$

in which $\gamma_{\mathrm{L}}^{\mathrm{LW}} = \gamma_{\mathrm{L}}$ if the liquid is apolar (or, more precisely, when there is no polar contribution to the liquid's energy of cohesion). In all cases, $\gamma_{\mathrm{L}}^{\mathrm{LW}}$ must be larger than $\gamma_{\mathrm{S}}^{\mathrm{LW}}$, so that the drop will not spread with zero contact angle.

II. Polar Systems

Equations (1)–(6) also describe the interaction between polar Polymers 1 and 2 dissolved in a polar Solvent 3, but the polar component of the interfacial tensions cannot be described by Eq. (8). First, it must be stressed that no substance is *completely* polar: all compounds are subject to apolar (Lifshitz-van der Waals) interactions. But polar compounds, in addition, undergo electron donor–electron acceptor (AB) interactions. In all electron donor–electron acceptor interactions, it must be realized that the electron-donor and the electron-acceptor parameters, in any one polar substance, are liable to be quantitatively quite different. Indeed, quite often, one of the parameters may be negligibly small and the other parameter rather large; such substances then may be called "monopolar" (*20*). The electron-acceptor parameter of the surface tension of a Substance *i* is designated as γ_i^+, and the electron-donor parameter of its surface tension as γ_i^-. The polar (Lewis acid-base or AB) component of the surface tension of that polar substance then is

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+\gamma_i^-} \tag{11}$$

With a monopolar substance, either γ_i^+ or γ_i^- is zero. Then, $\gamma_i^{AB} = 0$. The polar component of the interfacial free energy between Substances 1 and 2 is

$$\Delta G_{12}^{AB} \equiv -2(\sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}) \tag{12}$$

The interfacial tension between Substances 1 and 2 then can be expressed as

$$\gamma_{12}^{AB} = 2(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-} - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+}) \tag{13}$$

or as

$$\gamma_{12}^{AB} = 2(\sqrt{\gamma_1^+} - \sqrt{\gamma_2^+})(\sqrt{\gamma_1^-} - \sqrt{\gamma_2^-}) \tag{14}$$

From Eq. (15) it is clear that γ_{12}^{AB} will be negative when $\gamma_1^+ > \gamma_2^+$ and $\gamma_1^- < \gamma_2^-$, and when $\gamma_1^+ < \gamma_2^+$ and $\gamma_1^- < \gamma_2^-$.

In view of Eq. (7), it will be true that

$$\gamma = \gamma^{LW} + \gamma^{AB} \tag{15}$$

The total interfacial tension between Substances 1 and 2 then can be expressed as

$$\gamma_{12} = (\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}})^2 + 2(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-} - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+}) \tag{16}$$

From Eq. (16) and the Dupré equation (Eq. 2), the total interaction between polar Polymers 1 and 2 dissolved in polar Liquid 3 can therefore be expressed as

$$\Delta G_{132}^{\mathrm{TOT}} = \gamma_{12}^{\mathrm{LW}} - \gamma_{13}^{\mathrm{LW}} - \gamma_{23}^{\mathrm{LW}} + 2[\sqrt{\gamma_3^+}(\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} - \sqrt{\gamma_3^-})]$$
$$+ [\sqrt{\gamma_3^-}(\sqrt{\gamma_1^+} + \sqrt{\gamma_2^+} - \sqrt{\gamma_3^+}) - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+}] \qquad (17)$$

The complete Young-Good-Girifalco-Fowkes equation for polar systems is

$$(1 + \cos\theta)\gamma_{\mathrm{L}} = 2(\sqrt{\gamma_{\mathrm{S}}^{\mathrm{LW}}\gamma_{\mathrm{L}}^{\mathrm{LW}}} + \sqrt{\gamma_{\mathrm{S}}^+\gamma_{\mathrm{L}}^-} + \sqrt{\gamma_{\mathrm{S}}^-\gamma_{\mathrm{L}}^+}) \qquad (18)$$

The spreading pressure term pertaining to Eq. (18) will here be neglected.

MATERIALS AND METHODS

The surface tension values of the various solvents for use in our calculations were generally taken from the literature. In a few cases in which doubts as to purity arose, the values were verified by means of the Wilhelmy technique (*23*). The surface tension of diiodomethane was earlier found to be 50.8 mJ/m^2 (*13*), contrary to the value found in Ref. *22* (which is probably one of the very rare printing errors in that work).

Advancing contact angles were measured (*24*) at 20°C on various solids with the help of Teflon Gilmont syringes and a Gaertner goniometer attached to a Gaertner X-Y device, fixed to an optical bench. The liquids used for the contact angle measurements on polymer surfaces are characterized in Table 1 as to their $\gamma_{\mathrm{L}}^{\mathrm{LW}}$, γ_{L}^+, and γ_{L}^- values. Table 2 gives the same characteristics for the organic solvents used in this work. The surface tension parameters of the various solids are given in Table 3. These were determined by contact angle measurements on flat, smooth layers of the polymer in question, obtained by depositing a solution of the polymer in an appropriate solvent on a glass slide, and allowing the solvent to evaporate. It is clear from Eq. (18) that it is necessary to measure contact angles with at least three different completely characterized liquids to solve Eq. (18) for the three unknowns $\gamma_{\mathrm{S}}^{\mathrm{LW}}$, γ_{S}^+, and γ_{S}^-.

Phase separation data (i.e., mixing or separation) for various polymer pairs in given solvents were taken from earlier work (*6*) in many instances, but were redone (as described in Ref. *6*) in a number of doubtful cases and also in the case of polystyrene and polymethyl methacrylate dissolved in chloroform. As in the cases already discussed in Ref. *6*, phase separation, either visible with the naked eye or microscopically, would occur within 4 days at polymer concentrations of up to 6% (w/v). When after that lapse of time no phase separation could

TABLE 1

Surface Tension Parameters of Liquids Used in Contact Angle Determinations (in mJ/m^2)

Liquid	γ	γ^{LW}	γ^{AB}	γ^+	γ^-
Water	72.8[22]	21.8[25]	51[13]	25.5[a]	25.5[a]
Dimethylsulfoxide	44[16]	41	3[16]	0.07	35[16]
Diiodomethane	50.8[8]	50.8	0	0.7[b]	0
α-Bromonaphthalene	44.4[22]	43.6	0.8	0.4[c]	0.4[c]
Glycerol	64[22]	34[8]	30[8]	5.67[16d]	37.7[16d]

[a] These values are assumed; they are not known with any certainty. The assumption of such values may be obviated by using known γ_1^+/γ_2^+ and γ_1^-/γ_2^- ratios; via the use of these (known) ratios, γ_{12}^{AB}, and all ΔG^{AB} values can be obtained. These values then are the same as those obtained via the above assumption. In order to express γ^+ and γ^- values in S.I. units, the assumption of a γ^+/γ^- ratio for water remains necessary, however, and it should be noted that all γ^+ and γ^- values given here and in the following tables are based on the premises we made for water.

[b] From the interfacial tension with water (*26*) and the assumption of γ^+ monopolarity.

[c] From the interfacial tensions with water (*26*) and an assumption that $\gamma^+ \approx \gamma^-$ for this liquid in the absence of further data.

[d] More recently somewhat better values were obtained for glycerol, i.e., $\gamma^+ \approx 3.92$, $\gamma^- \approx 57.4$.

TABLE 2

Surface Tension Parameters of Organic Liquids Used (in mJ/m^2)

Liquid[a]	γ	γ^{LW}	γ^{AB}	γ^+	γ^-
MEK	24.6[b]	24.6			24[f]
CHX	25.24[b]	25.24			
CTC	26.8[b]	26.8[b]			
CFO	27.3[b]	27.3[b]		3.8[d]	
THF	27.4[b]	27.4[b]			15.0[g]
TOL	28.3[b]	28.3[b]			2.7[d]
BNZ	28.9[b]	28.9[b]			2.3[d]
CBNZ	33.6[b]	32.1	1.5[c]	0.9[e]	0.61[e]
NBNZ	43.9[b]	41.3	2.6[c]	0.26[e]	6.6[e]

[a] Abbreviations: methyl ethyl ketone, MEK; cyclohexane, CHX; carbon tetrachloride, CTC; chloroform, CFO; tetrahydrofuran, THF; toluene, TOL; benzene, BNZ; chlorobenzene, CBNZ; nitrobenzene, NBNZ.

[b] Ref. *22*.

[c] From contact angle determinations on Teflon; i.e., 62° for CBNZ and 75° for NBNZ.

[d] From the interfacial tension with water (*26*) and the assumption of monopolarity; see Eq. (16).

[e] From the interfacial tension with water (*26*) and γ^{AB}; see Eqs. (11) and (16).

[f] Average of the maximum value of 27.9 and the minimum value of 20.4 mJ/m^2; see text and Table 6.

[g] Average of the maximum value of 19.4 and the minimum value of 10.5 mJ/m^2; see text and Table 6.

TABLE 3
Surface Tension Parameters of the Polymers Used (in mJ/m^2)

Polymer[a]	γ	γ^{LW}	γ^{AB}	γ^+	γ^-
PIB	25[b]	25[b]			
PPL	25.7[c]	25.7[c]			
CLA	43	38[g]	5.2	0.3[g]	22.7[g]
PMMA	40.6[d]	40.6[d]			12.0[d]
PST	42[e]	42[e]			1.1[i]
PVC	43.8	43[f]	0.75	0.04[h]	3.5[h]

[a] Abbreviations: polyisobutylene, PIB; polypropylene, PPL; cellulose acetate, CLA; polymethyl methacrylate, PMMA; polystyrene, PST; polyvinyl chloride, PVC.

[b] From $\theta = 60°$ with α-bromonaphthalene.

[c] From $\theta = 58.5°$ with α-bromonaphthalene.

[d] From Ref. *13*.

[e] From Ref. *27*.

[f] From $\theta = 15°$ with α-bromonaphthalene.

[g] From $\theta = 58°$ with water, $\theta = 56.5°$ with glycerol, and $\theta = 20°$ with dimethylsulfoxide.

[h] From $\theta = 82.5°$ with water and $\theta = 68°$ with glycerol.

[i] From $\theta = 91.4°$ with water; Ref. *28*.

be observed in a given system either macroscopically or microscopically, compatibility (*6*) (or miscibility) was assumed to exist. A few data from the earlier paper (*6*) were not reconsidered; i.e., polymers dissolved in dichlorobenzene and in cyclohexanone, because of an absence of data on the polar parameters of the surface tension of these liquids. The polar parameters of the surface tension of methyl ethyl ketone and of tetrahydrofuran were also unknown, but could be estimated rather closely from this work (see below).

RESULTS

Table 4 lists the ΔG_{132}^{TOT} values and the miscibility vs separation characteristics of apolar systems, and in Table 5 those of a few polar systems are listed. It should be noted that most of the polymers as well as most of the solvents of the systems treated as apolar do have some polar characteristics, but these were all of a monopolar nature, involving monopoles of the same sign, such that the entire polar part of the right-hand term of Eq. (10) remained zero, leaving only the three first (LW) right-hand terms. Table 5 also comprises a number of monopoles (solid

TABLE 4
$\Delta G_{132}^{\mathrm{TOT}}$ Values and Miscibility vs Separation in Apolar Systems

System	$\Delta G_{132}^{\mathrm{TOT}}$ (in mJ/m^2)	Observation
1. PMMA and PST in MEK	−3.7	Miscible
2. PMMA and PST in THF	−2.8	Miscible
3. PMMA and PST in BNZ	−2.2	Miscible
4. PIB and PST in BNZ	+0.8	Separation
5. PIB and PMMA in BNZ	+0.8	Separation
6. PIB and PST in TOL	+0.7	Separation
7. PIB and PST in THF	+0.6	Separation
8. PIB and PMMA in THF	+0.5	Separation
9. PIB and PST in CTC	+0.4	Separation

and liquid) but these involve interactions between polarities of *opposite signs,* which strongly impact on the right-hand side of Eq. (17).

While the surface tensions of MEK and THF are known with precision (*22*), their γ^- components are not. From contact angle measurements on Teflon it could be ascertained that for both liquids, $\gamma \approx \gamma^{\mathrm{LW}}$, i.e., their $\gamma^{\mathrm{AB}} \approx 0$. They nevertheless have a sizable γ^- parameter, e.g., by analogy with the measured value for dimethylsulfoxide (*16*). Measurement of the γ^- of these liquids by contact angle measurements on solids with a known γ^+ is not feasible because the γ_{L} of both liquids is significantly smaller than the γ_{S} of available polar solids, which thus would lead to spreading. Encasing these liquids in a gel, as was done with, e.g., dimethylsulfoxide (*16*), while

TABLE 5
$\Delta G_{132}^{\mathrm{TOT}}$ Values and Miscibility vs Separation in Polar Systems

System	$\Delta G_{132}^{\mathrm{LW}} + \Delta G_{132}^{\mathrm{AB}} = \Delta G_{132}^{\mathrm{TOT}}$ (in mJ/m^2)	Observation
10. PIB and PPL in CBNZ	$-0.8 - 4.6 = -5.4$	Miscible
11. PMMA and PST in NBNZ	$+0.006 - 0.6 = -0.6$	Miscible
12. PIB and PST in CBNZ	$+1.1 - 1.0 = +0.1$	Separation
13. PIB and PVC in CBNZ	$+1.2 + 2.0 = +3.2$	Separation
14. PMMA and PST in CBNZ	$-1.1 + 5.7 = +4.6^{a,*}$	Separation
15. PMMA and PST in CFO	$-2.9 + 17.7 = 14.8^{*}$	Separation

[a] No separation was observed at 6.6% $(w/v)^2$, but separation occurred at ≈10% (w/v).

*If it were not for the AB interactions, miscibility would have prevailed in these cases.

possible, would not lead to a measurable contact angle with other liquids on account of the adverse effects of the volatility of both MEK and THF. Thus the present method of estimating the γ^- values of these liquids from phase separation data may, for the moment, be the only feasible approach; see Table 6. The importance of taking ΔG_{132}^{AB} into account in predicting phase separation is indicated by an asterisk (Tables 5 and 6, polymer pairs 14, 15, 22, and 23); in these cases the observed separation would not have been predicted from the ΔG_{132}^{LW} alone.

All nine apolar systems listed in Table 4 show a complete correlation between a negative ΔG_{132} and mixing, and a positive ΔG_{132} and separation. There is also complete correlation with the polar systems listed in Table 5. Of the systems pertaining to MEK and THF, Nos. 20 to 23 were used to determine the limits for the γ^- values of MEK and THF (see Table 6). In the six systems shown in Table 5, the systems' surface tension parameters of the polymers as well as of the solvents were determined independently of the outcome of the phase separation (or miscibility) observations. It thus would seem that not only in exclusively apolar systems, but also in polar systems, phase separation of polymer pairs dissolved in the same organic solvent conforms to the surface thermodynamic treatment we developed for polar systems (*8*, *14–20*). The same treatment could also successfully account for the mechanism of phase separation in aqueous systems (*8*, *14*).

TABLE 6
ΔG_{132}^{TOT} Values and Miscibility vs Separation in Polar Systems with MEK and THF as Solvents

System	ΔG_{132}^{LW} + (in mJ/m^2)	ΔG_{132}^{AB} =	ΔG_{132}^{TOT}	Observation
16. PMMA and PVC in THF	−3.0 −	0.7 =	−3.7	Miscible
17. PST and PVC in MEK	−4.9 +	1.6 =	−3.3	Miscible
18. PMMA and PVC in MEK	−3.0 +	0.6 =	−2.4	Miscible
19. PST and PVC in THF	−3.3 +	1.2 =	−2.1	Miscible
20. CLA and PVC in THF[a]	−2.4 +	1.7 =	−0.7	Miscible
21. CLA and PVC in MEK[b]	−3.8 +	3.3 =	−0.5	Miscible
22. CLA and PST in MEK[c]	−3.7 +	4.1 =	+0.4[e]	Separation
23. CLA and PST in THF[d]	−2.3 +	3.0 =	+0.7[e]	Separation
24. PIB and CLA in THF	+0.5 +	4.1 =	+4.6	Separation

[a] γ^- must be less than 19.4 mJ/m^2
[b] γ^- must be less than 27.9 mJ/m^2
[c] γ^- must be more than 20.4 mJ/m^2
[d] γ^- must be more than 10.5 mJ/m^2

for the sign of ΔG_{132}^{AB} to be in accordance with the observation.

[e] If it were not for the AB interactions, miscibility would have prevailed in these cases.

DISCUSSION

A comparison was made between the results published earlier (*6*) and the systems that have been reinvestigated here. To begin with, the surface tensions of the *solvents* found earlier are much the same as those given here, with only minor corrections (see Table 2). The values for the total surface tensions (γ) of the *polymers*, however, often differed from those found by the more accurate methods used in this work. If our present values for the γ of the polymers had been used in the earlier work, the correlation with phase separation found (still using just Eq. 1) would not at all have been as satisfactory as was then believed (*6*). That decrease in correlation would have been partly due to erroneous γ-values of the polymers and partly due to the fact that, as already stated in the Introduction, the lumping of apolar and polar interestions into one single factor is simply too much of an oversimplification. Also, as can be seen from the Young-Good-Girifalco-Fowkes Eq. (18), to solve for the three independent surface tension parameters γ_S^{LW}, γ_S^+, and γ_S^- of any given solvent, Eq. (18) must be used *three times* by contact angle measurements with three significantly different liquids. In view of this new treatment, there was little likelihood that a single "equation of state" (*29*) could have succeeded in embracing all three independently variable parameters in one equation. In addition, the "equation of states" computer program (*29*) comprises the impossibility for the interfacial term to become negative, although, as is clear from Eq. (16), the interfacial tension of polar systems can quite readily, and indeed does quite frequently, become negative (*15*, *20*). Hence the errors that tend to occur in the γ_S values measured with single and very polar liquids, such as water. Thus, in the earlier work (*6*), errors of interpretation of contact angles, combined with an unfelicitous choice of contact angle liquid, were evened out by flaws in the computation of interfacial interaction energies in polar systems.

While older explanations based on osmotic interactions (*30*) are not overly cogent [as Molyneux (*7*) concluded from the results obtained in aqueous systems, given in Ref. *30*, an actual repulsion between the dissolved polymer appeared to exist over and above their osmotic interaction], Albertsson's proposition that *a repulsive interaction must occur between unlike molecules* (*2*), although somewhat vague, remains true, and must be considered as the crucial basis for any more detailed explanation. In wholly apolar systems, this is precisely what happens: In apolar systems two varieties of fairly similar polymer molecules attract each other (but not enough to cause precipitation) and thus are miscible, while more dissimilar polymer molecules repel each other, which leads to phase separation (*6*) (see Table 4). However, in strongly polar systems, e.g., in aqueous phase separation, even rather similar polymer molecules can repel one another (*2*), but the energies of repulsion between Polymer molecules 1 and 1 are not quite the same as the repulsion energies between Polymer molecules 2 and 2. Such a condition can give rise to phase separation (*8*) by a mechanism which may be described as follows: In water (3), Polymer molecules 1 repel each other with energy ΔG_{131} and Polymer molecules 2 repel each other with energy ΔG_{232}, while Polymer molecules 1 and 2 repel each other with energy ΔG_{132}, in such a manner that when, e.g., $\Delta G_{131} > \Delta G_{232}$, then also $\Delta G_{131} > \Delta G_{132} > \Delta G_{232}$. Such a system will only come to equilibrium after a sorting-out, i.e., when Polymers 1 have congregated to one phase and Polymers 2 to the other phase, to which effect it also is necessary that $\Delta G_{132} > 1.5$ kT; see Fig. 1. This usually first tends to give rise to an emulsion-like phase separation of droplets of one phase suspended in the other phase; usually the droplets then gradually coalesce and two distinct phases are formed with typically a markedly small interfacial tension between the two phases of the order of 10^{-4} to 10^{-1} mJ/m^2. In polar systems the driving force for the phase separation, or for microemulsion formation (*20*), would be the initial negative interfacial tension, which increases to a value close to zero (*20*) upon attaining equilibrium, at which value it levels off.

Thus, the major condition for a phase separation to occur in a solution containing two different solutes (of which one, in general, is a macromolecule) dissolved in the same solvent is that the free energy of interaction between Solutes 1 and 2 while dissolved in Solvent 3 must have a positive value, i.e., $\Delta G_{132} > 0$. This condition ensures that the dissolved Solutes 1 and 2 repel each other while immersed in Solvent 3. However, this condition does not automatically guarantee phase separation, for as long as the thermal motion energy of the dissolved (macro-) molecules is large enough to match the energy of interaction between dissolved Molecules 1 and 2, any separation that might occur would be undone by thermal remixing. Separation therefore can only prevail over remixing when $\Delta G_{132} > +1.5$ kT, where ΔG_{132} is expressed in terms of free energy of interaction between (macro-)Molecules 1 and 2 *per unit area of contactable surface.* The second condition clearly can only be fulfilled (at a given temperature T) when at least one of the solutes has a minimum molecular weight, to ensure reaching the required contactable surface area. And it also can only be fulfilled when a critical minimum concentration of Solutes 1 and 2 has been reached to ensure: a) a sufficient likelihood of repulsive encounters, and b) a sufficient degree of desolvation of the macromolecules to allow for interactions between

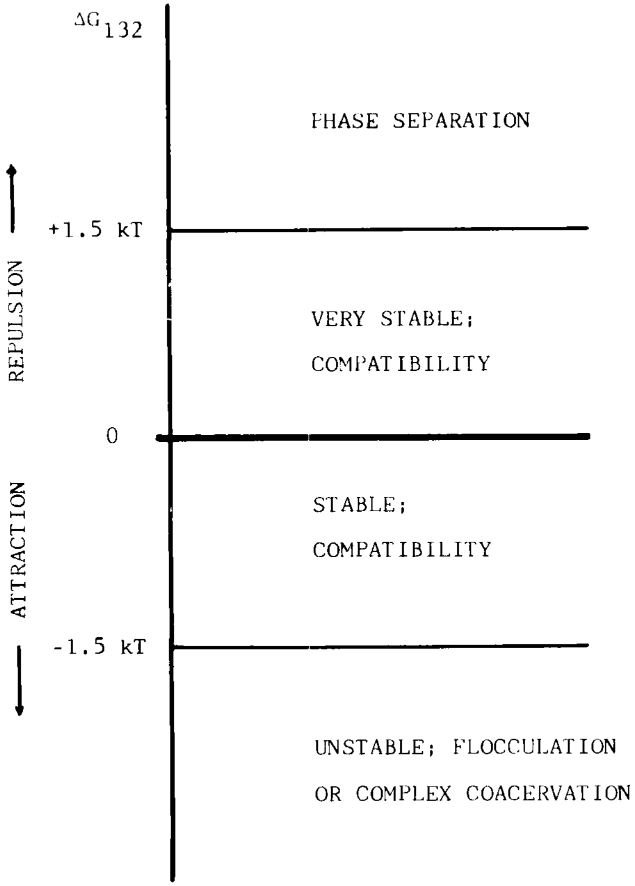

FIG. 1. Schematic presentation of the four categories of values ΔG_{132} (of a solution of Polymer pairs 1 and 2 in Solvent 3) can assume (in multiples of ±1.5 kT), expressed in energy per unit of average contactable surface area between two polymer molecules.

macromolecules that are not largely masked by excessively thick layers of molecules of solvation (*8*). It should be noted that the mutual repulsion of all solutes in a polar system makes it possible for such a system to split into multiple phases, i.e., as many phases as there are different macrosolutes (*2*). Apolar systems, however, cannot give rise to more than two phases.

Thus, clearly, temperature as well as solute molecular weight and concentration play a crucial role in phase separation, but the *conditio sine* *qua non* is a repulsion between the two different solutes, i.e., a positive value of ΔG_{132}.

The present results appear to put the thesis that polymer phase separation (in apolar as well as in polar systems) is quantitatively predictable via a determination of a system's interfacial interaction energy on a more solid basis. It also appears possible to use polymer phase separation results for the determination of the upper and lower limits of the polar surface tension parameter(s) of low energy liquids. Thus, for MEK, $\gamma^{-} \approx 24.2 \pm 3.7$, and for THF, $\gamma^{-} \approx 15.0 \pm 4.5$ (mJ/m^2) could be estimated (see Table 6).

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