Interfacial tension and interaction parameters

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(Received 5 April 1994)

In view of various contradictory theoretical equations relating the interfacial tension σ between phase-separated polymer solutions to the Flory–Huggins interaction parameter of the system, the idea that σ should depend on the extent of the 'hump' in the concentration dependence of the Gibbs energy of mixing was studied. This investigation is based on 12 series of $\sigma(T)$ measurements reported in the literature and on additional experiments for the system cyclohexane/polystyrene. To quantify the extent of the 'hump', a reduced 'hump energy' ε was introduced and its value calculated for different temperatures from the measured critical data of the systems. The analysis of the entire experimental material yields a scaling law of the form $\sigma = E\varepsilon^F$ where F is close to 0.5 for all systems, in contrast to E which varies within a larger interval. Furthermore, ε is related to τ, the relative distance to the critical temperature, by $\varepsilon = A\tau^B$; B is approximately 2.4, again relatively independent of the system, in contrast to A. In case of trustworthy values of the scaling parameters, the above relations offer an interesting possibility to estimate $\sigma(T)$ from the sole knowledge of the critical temperature of the system.

(Keywords: interfacial tension; Flory–Huggins parameter; polymer solutions)

INTRODUCTION

Numerous theoretical attempts[1–6] have been made to calculate the interfacial tension between coexisting liquid phases of binary systems from the interaction parameters measuring the mixing tendency of the components. A central point of these approaches is the gradient of composition within the interfacial layer keeping the chemical potentials in this transition zone identical with those in the bulk phases, in spite of local concentrations which lie inside the miscibility gap.

For polymer solutions[2–5] and polymer mixtures[5,6] several equations relating the interfacial tension σ to the Flory–Huggins interaction parameter[7] χ are reported in the literature. In all cases, however, the derivation of these relations starts with very stringent assumptions, such as concentration independent interaction parameters or a certain mathematical form of the concentration profile. It can therefore hardly be expected that they correctly describe reality.

The present contribution investigates whether a phenomenological treatment, avoiding these restrictions, could improve the situation and yield reliable additional information. In particular it is investigated how the interfacial tension depends on the size of the 'hump' in ΔG_{mix}, the molar Gibbs energy of mixing, as a function of x_2, the mole fraction of the polymer. The idea behind this statement of the problem is this: since $\Delta G_{\mathrm{mix}}(x_2)$ determines the composition of the coexisting phases and the concentration profile within the interfacial layer, the size of the hump should also be closely related to σ. For the following discussion the 'hump' energy is, like σ itself, treated as an experimental quantity; it is calculated from the measured phase diagram of the system by adjusting $\chi(x_2, T)$ using an arbitrarily chosen function.

DATA TREATMENT

The data required for the above-mentioned discussion were mainly taken from the literature and refer to narrowly distributed polymer samples in all cases. The best studied system is methyl cyclohexane/polystyrene (MCH/PS)[8–10]; valuable information is also available for phenetol/poly(dimethyl siloxane) (PTL/PDMS)[11]. Some additional measurements were performed with the system cyclohexane/polystyrene (CH/PS)[12]. The anionically polymerized PS was purchased from PSS (Mainz; Germany); its molar mass is 96 kg mol^{-1} and M_w/M_n is 1.04. The experimental procedure for the determination of the cloud-point curve and of the interfacial tension (spinning-drop method) was the same as described in reference 9. The newly obtained σ values can be read from *Figure 1* as a function of $\tau = (T_c - T)/T_c$, the relative distance to the critical temperature. This diagram also contains examples for the behaviour of the two other systems under investigation.

In order to obtain information on the hump in $\Delta G_{\mathrm{mix}}(x_2)$, the critical data, i.e. T_c and φ_{2c} (volume fraction of the polymer) were evaluated on the basis of $\bar{G}_{\mathrm{mix}}$, the

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0032-3861/94/26/5743–05

segment molar Gibbs energy of mixing, according to

$$\left(\frac{\partial^2 \bar{\bar{G}}_{\mathrm{mix}}/RT}{\partial \varphi_2^2}\right)_c = 0 \quad \left(\frac{\partial^3 \bar{\bar{G}}_{\mathrm{mix}}/RT}{\partial \varphi_2^3}\right)_c = 0 \tag{1}$$

formulating the partial Gibbs energies of mixing of the solvent ($\Delta\mu_1$) and of the polymer ($\Delta\mu_2$) in terms of the Flory–Huggins equations[7]

$$\Delta\mu_1/RT = \frac{1}{r_1}\ln(1-\varphi_2) + \left(\frac{1}{r_1} - \frac{1}{r_2}\right)\varphi_2 + \ln f_1 \tag{2}$$

$$\Delta\mu_2/RT = \frac{1}{r_2}\ln(\varphi_2) + \left(\frac{1}{r_2} - \frac{1}{r_1}\right)(1-\varphi_2) + \ln f_2 \tag{3}$$

where r_i are the numbers of segments, defining a segment in terms of a molar volume of 100 cm^3 mol^{-1}, and f_i are the activity coefficients. For the solvent the latter quantity is related to the Flory–Huggins parameter χ by

$$\ln f_1 = \chi\varphi_2^2 \tag{4}$$

In order to represent the measured phase diagram mathematically it is necessary to establish some function $\chi(\varphi_2, T)$ that is apt to produce the humps in $\Delta G_{\mathrm{mix}}(x_2)$ such that the double tangent yields the correct composition of the coexisting phases at the different temperatures. Tests with several relations have demonstrated that the simplest possible Ansatz that meets this requirement is

$$\ln f_1 = \frac{\beta(1-p)}{T(1-p\varphi_2)^2}\varphi_2^2 \quad \ln f_2 = \frac{\beta}{T(1-p\varphi_2)^2}(1-\varphi_2)^2 \tag{5}$$

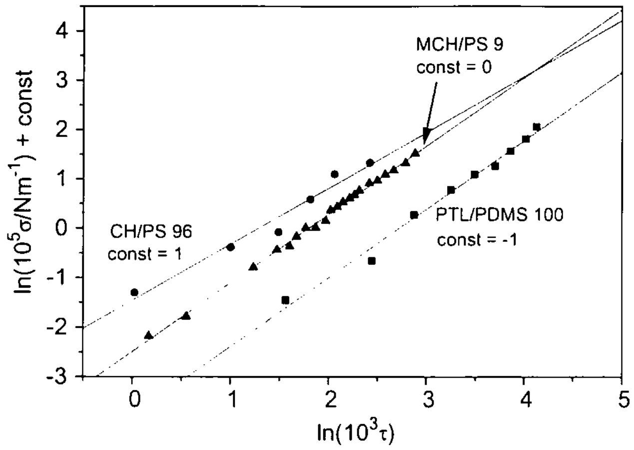

Figure 1 Interfacial tension σ as a function of $\tau = (T_c - T)/T_c$, the relative distance to the critical temperature for the indicated systems. More information can be obtained from *Table 1*

By means of the parameters β and p (describing the temperature and concentration dependence of the Flory–Huggins parameter) plus relations (2) and (3) it is possible to reproduce the phase diagrams of all systems under consideration within experimental error in the temperature range of interest. The values of β and p of the different systems can be easily obtained by means of equation (1) from the measured critical data.

Table 1 collects all relevant data. The agreement of the information concerning the critical temperatures for the system MCH/PS stemming from different sources is quite satisfactory as can be seen in the Shultz–Flory plot[13] of *Figure 2*. The extrapolated Θ temperature is in good accord with that reported in the literature[14].

THEORY AND DISCUSSION

As a measure for the size of the hump in $\Delta G_{\mathrm{mix}}(x_2)$, the reduced hump energy ε is introduced in terms of the segment molar Gibbs energy of mixing $\bar{\bar{G}}_{\mathrm{mix}}$ according to the relation

$$\varepsilon = \frac{1}{RT}\int_{\varphi_2'}^{\varphi_2''}\left\{\left[\frac{\bar{\bar{G}}_{\mathrm{mix}}(\varphi_2') - \bar{\bar{G}}_{\mathrm{mix}}(\varphi_2'')}{\varphi_2' - \varphi_2''}\right]\varphi_2 + \bar{\bar{G}}_{\mathrm{mix}}(\varphi_2'') - \left[\frac{\bar{\bar{G}}_{\mathrm{mix}}(\varphi_2') - \bar{\bar{G}}_{\mathrm{mix}}(\varphi_2'')}{\varphi_2' - \varphi_2''}\right]\varphi_2'' - \bar{\bar{G}}_{\mathrm{mix}}(\varphi_2)\right\}\mathrm{d}\varphi_2 \tag{6}$$

How the quantity ε is calculated can be seen from *Figure 3* which shows the area defining the reduced hump energy.

Since the present considerations are confined to near-critical conditions, the interdependencies are, as

Table 1 Compilation of the systems under investigation, their critical temperatures T_c and critical volume fractions φ_{2c} plus the thermodynamic parameters β and p (equation (5)) calculated therefrom (equation (1))

No.	Ref.	Solvent	Polymer[a]	T_c (K)	φ_{2c}	β (K)	p
1	8	MCH	PS 9.0	281.20	0.199	221.18	0.3151
2	9	MCH	PS 17.5	296.05	0.169	227.14	0.3140
3	8	MCH	PS 17.5	296.32	0.160	227.35	0.3141
4	8	MCH	PS 37.0	309.65	0.125	232.03	0.3087
5	10	MCH	PS 37.0	309.65	0.131	233.63	0.3152
6	9	MCH	PS 42.5	311.55	0.121	234.32	0.3165
7	9	MCH	PS 86.3	320.05	0.096	238.45	0.3152
8	8	MCH	PS 110.0	323.24	0.088	241.27	0.3189
9	9	MCH	PS 175.0	326.65	0.071	241.07	0.3129
10	8	MCH	PS 233.0	329.93	0.059	241.77	0.3089
11	8	MCH	PS 1260.0	336.97	0.028	244.58	0.3074
12	11	PTL	PDMS 100.0	341.09	0.105	258.97	0.3314
13	12	CH	PS 96.0	293.65	0.075	211.83	0.2886

[a] The number represents molecular weight, M (kg mol^{-1})

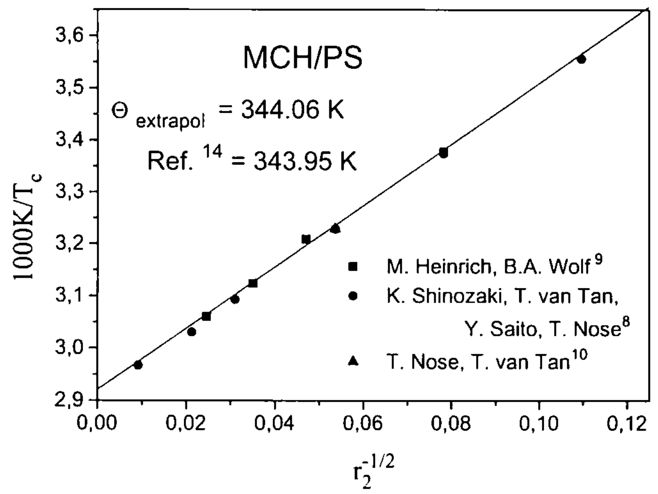

Figure 2 Shultz–Flory plot[13] for the system MCH/PS; r_2 is the number of segments of the polymer ($100\,cm^3/mol$ each)

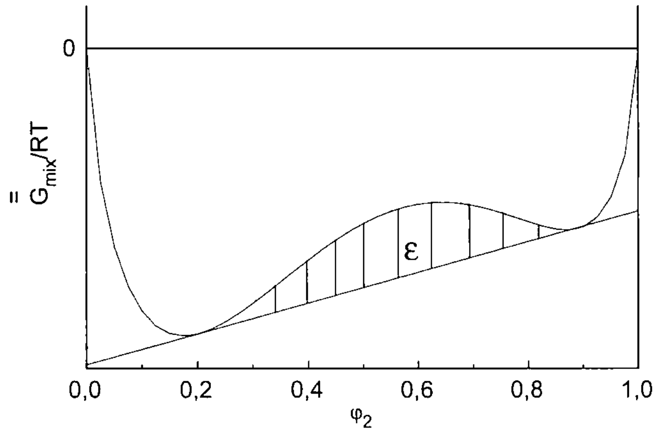

Figure 3 Scheme demonstrating the calculation of the reduced hump energy ε from the variation of $\bar{G}_{mix}$, the segment molar Gibbs energy of mixing, with φ_2, the volume fraction of polymer

usual, formulated in terms of scaling laws[15]. First it is investigated whether ε as a function of τ obeys the relation

$$\varepsilon = A\tau^B \tag{7}$$

which is written by analogy to

$$\sigma = C\tau^D \tag{8}$$

For D (often named μ) theoretically derived values have already been reported. Finally it is investigated whether a law similar to equation (8) can be used to describe σ as a function of ε

$$\sigma = E\varepsilon^F \tag{9}$$

The following relations between the different parameters hold true

$$C = EA^F \tag{10}$$

$$D = BF \tag{11}$$

Equation (7) is well fulfilled for all polymer solutions under investigation as can be seen from the examples shown in *Figure 4*.

The validity of equation (8) has already been demonstrated in *Figure 1*. *Figure 5* proves that indeed $\sigma(\varepsilon)$ can be formulated by a scaling law (equation (9)). *Figure 5* gives some typical examples, including one for a system (PTL/PDMS) for which the distance to the critical condition is rather large so that a systematic deviation from linearity can already be noticed. All parameters resulting from the evaluation of data according to equations (7) to (9) are collected in *Table 2*.

The critical exponents B, D and F result independent of the chemical nature of the systems within experimental error. The factors A, C and E, on the other hand, vary considerably; from earlier measurements[9] it can be inferred that they should depend on the molar mass of the polymer. Although there is a tendency for these parameters to diminish as M is raised, no clear-cut dependence is noticeable within experimental error; the parameter A, for which the correlation is best, decreases with approximately the inverse third root of M. In spite of these chain length dependencies of A, C and E, average values are reported for all characteristic parameters of the 10 representatives of the system MCH/PS, together with the corresponding standard deviations. The critical exponents D of $\sigma(\tau)$ lie between that resulting from the

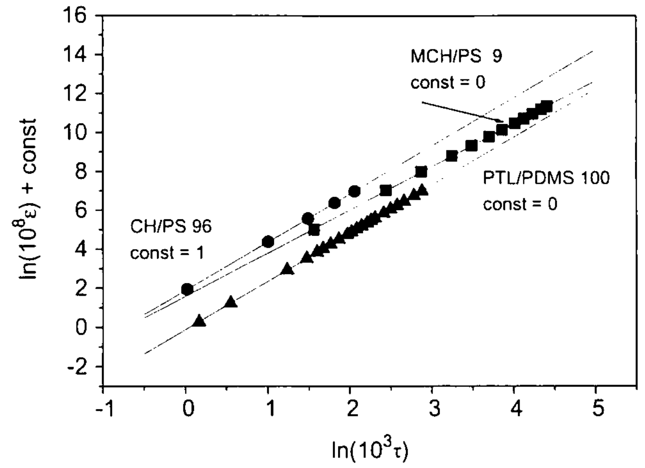

Figure 4 Interdependence of the reduced hump energy ε (equation (6)) and $\tau = (T_c - T)/T_c$ (T_c is the critical temperature) evaluated according to equation (7)

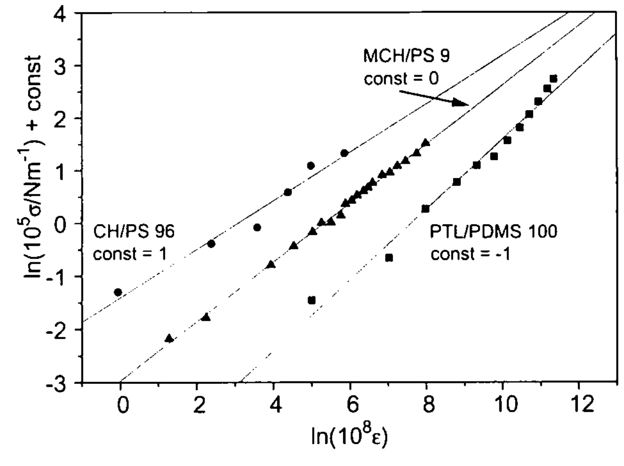

Figure 5 Interdependence of the interfacial tension σ and the reduced hump energy ε (equation (6)) evaluated according to equation (9)

Table 2 Parameters of the scaling laws formulated in equations (7)–(9) for the different systems, given the same numbers as in *Table 1*. In the calculation of the averages for the system MCH/PS, the σ values of no. 6 are not taken into consideration because of the large discrepancies with the rest of the information

	$\varepsilon(\tau)$		$\sigma(\tau)$		$\sigma(\varepsilon)$	
No.	A	B	10^3C (N m^{-1})	D	10^3E (N m^{-1})	F
1	0.622	2.470	11.91	1.386	15.52	0.561
2	0.464	2.420	8.91	1.400	13.97	0.579
3	0.684	2.500	12.15	1.390	15.06	0.556
4	0.408	2.410	4.26	1.229	6.62	0.509
5	0.412	2.412	3.92	1.210	6.06	0.501
6	0.376	2.392	(30.80)	(1.694)	(61.35)	(0.708)
7	0.259	2.349	2.87	1.248	5.86	0.531
8	0.332	2.388	2.78	1.210	4.81	0.506
9	0.215	2.364	2.50	1.286	5.78	0.544
10	0.204	2.396	4.81	1.444	12.44	0.602
11	0.159	2.482	5.85	1.202	1.41	0.484
average	0.376	2.417	6.00	1.300	8.70	0.537
±	0.16	0.046	3.50	0.090	4.70	0.035
12	0.213	2.213	13.10	1.477	36.85	0.667
13	0.226	2.466	4.87	1.287	10.60	0.522

Table 3 Dependence of the thermodynamic parameters β and p (equation (5)) and of the parameters E and F (equation (9)) on the variation of the critical temperatures T_c and of the critical volume fraction φ_{2c} for the system CH/PS

T_c (K)	φ_{2c}	p	β (K)	10^3E (N m^{-1})	F
293.65	0.075	0.2886	211.83	10.6	0.522
294.15	0.075	0.2886	212.19	11.1	0.522
293.15	0.075	0.2886	211.47	11.1	0.522
293.65	0.070	0.2779	209.19	11.2	0.514
293.65	0.080	0.2975	214.09	9.4	0.519

mean-field theory[1,16] (1.50) and the Ising[17] value (1.26) within the standard deviation stated in *Table 2*.

For the assessment of the reliability of the obtained critical exponents it was checked to what extent the results depend on errors in the measured critical data. *Table 3* gives some examples for the variation of p and β (equation (5)) and of E and F (equation (9)).

From the above compilation it becomes obvious that an uncertainty in T_c of ± 0.5 K remains far below the other experimental inadequacies. The difficulties in measuring the exact value of φ_{2c} turn out to be much more consequential. However, the changes in the parameters E and F resulting from an error of ± 0.005 in the volume fraction lie well inside the limits of the standard deviations reported in *Table 2*. The fact that erroneous φ_{2c} values alter E significantly whereas they do not change the critical exponent F markedly can be seen from *Figure 6*.

CONCLUSIONS

The results presented above demonstrate that there exists an unequivocal interrelation between the reduced hump energy ε and the interfacial tension σ. In order to test the possibilities this new information offers for the prediction of σ from the knowledge of the thermodynamic critical data of a system, the average values of E and F (see *Table 2*) were used to calculate σ as a function of $T_c - T$ for the system MCH/PS 37 (no. 5 in *Table 2*); this example was chosen because of the availability of theoretical calculations[3,10]. The ε required in equation (9) was obtained by means of the parameters β and p (no. 5 in *Table 1*). *Figure 7* shows these data together with the experimentally measured interfacial tensions and two theoretical predictions.

The better agreement of the values calculated from equation (9) with reality (despite the fact that the deviation of the average E and F values from the actual data is one of the largest) as compared with the theoretical results is not surprising in view of the fact that E and F already contain experimental information. Whether or not the newly presented scaling law is suitable for the prediction of σ depends on the generality of its parameters. So far it looks as if F would be on the order of 0.50, independent of the particular nature of the system; the situation

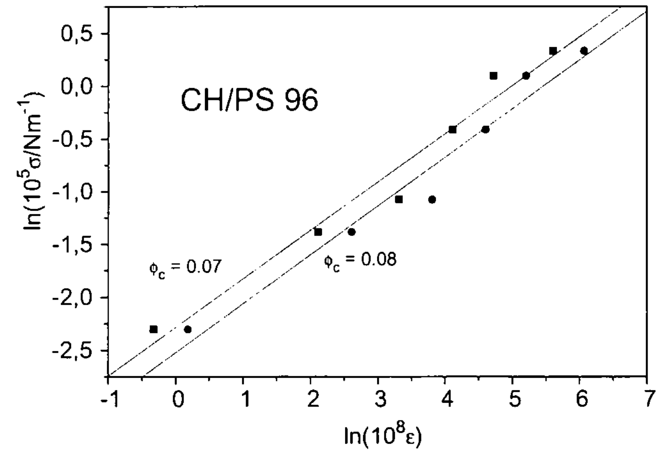

Figure 6 Interdependence of interfacial tension σ and the reduced hump energy ε for the system CH/PS 96, assuming an error in φ_{2c}, the critical volume fraction of the polymer, of ± 0.005. An uncertainty of ± 0.5 K in the critical temperature cannot be detected in this graph

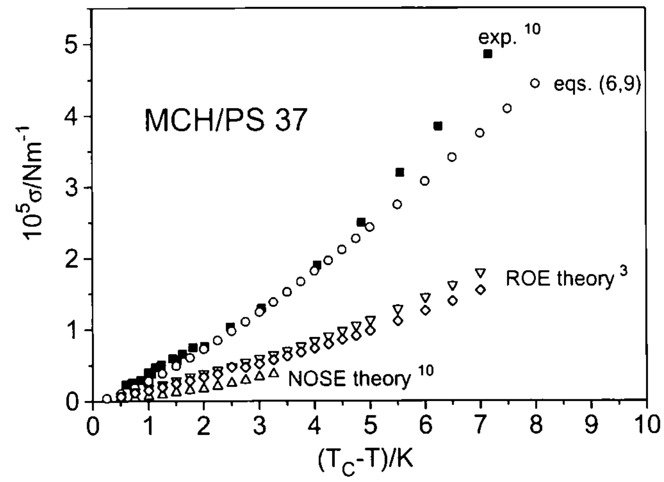

Figure 7 Comparison of the interfacial tensions σ measured for the system MCH/PS 37 with theoretical predictions[3,10] and with that calculated from equations (6) and (9) as described in the text. The larger values of Roe theory refer to 500 and the lower ones to 200 segments; according to the authors the actual number of segments of PS 37 lies between the above values

appears to be more complex with E since there exist indications that this parameter depends on M and on the chemical nature of the components.

It is noteworthy that good estimates of σ can already be made based on the mere knowledge of the critical temperature of the system by calculating ε from equation (7) and then the interfacial tension from equation (9) by means of the tabulated average parameters A and B plus E and F. Another interesting item concerns polymer blends. According to orienting studies these systems also obey scaling laws which are similar to those presented here for polymer solutions.

ACKNOWLEDGEMENTS

S. E. is grateful to the Deutsche Forschungsgemeinschaft for a Forschungsstipendium.

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