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PREFERENTIAL SOLVATION OF POLY(DIMETHYLSILOXANE) AND POLY(METHYL METHACRYLATE) IN BENZENE–METHANOL MIXTURES BY GEL PERMEATION CHROMATOGRAPHY

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SUMMARY

Preferential solvation λ parameters for the ternary systems benzene–methanol–poly(dimethylsiloxane) and benzene–methanol–poly(methyl methacrylate) have been determined by gel permeation chromatography. When benzene is preferentially adsorbed by the polymer, good agreement is found between λ values determined by this method and by light scattering and dialysis equilibrium. However, when methanol is preferentially adsorbed by the polymer, discrepancies arise. The differences are discussed in terms of interactions between the solvent and the chromatographic support.

INTRODUCTION

The preferential solvation of polymers in binary solvent mixtures has been studied by different physicochemical techniques, such as dialysis equilibrium[1], light scattering[2], ultracentrifugation[3] and densitometry[4], and spectroscopic techniques such as nuclear magnetic resonance[5], fluorescence inhibition[6] and infrared spectroscopy[7,8]. On the other hand, it is a known experimental fact that the frequent presence of vacant peaks in gel permeation chromatograms[9], when working with mixed solvents. In this case, as Berek *et al.*[10] have recently shown, if the magnitude of the vacant peak is proportional to the amount of polymer injected and its elution volume corresponds to that of one of the components of the mixture, the quantitative evaluation of the preferential solvation parameter becomes possible.

In this paper we report results on the determination of the preferential solvation parameter by gel permeation chromatography (GPC). Two ternary systems, the preferential adsorption of which has been established by classical techniques, have been chosen to test the reliability of the GPC method. The systems are poly(dimethylsiloxane)–benzene–methanol[4] and poly(methyl methacrylate)–benzene–methanol[11]. The second of these systems seemed to us of particular interest due to the appearance of an inversion in its preferential solvation.

EXPERIMENTAL

All of the measurements were carried out on a commercial Waters Assoc., Model ALC/GPC 202 liquid chromatograph, equipped with a 6000-p.s.i. pump, a differential refractometer unit R401 and a U6K universal injector, admitting sample sizes from 1 μl up to 2 ml. The differential refractometer cell was thermostatted at 22.0° and the elution volumes were determined from the weight of eluent. The solvent reservoir and the waste container were connected in order to avoid changes in mixture composition. The constancy in mixture composition was tested by refractometry. A Pharmacia SR 25 column (45 × 0.25 cm I.D.) packed with Spherosil XOA 200 of high granularity (100–200 μm) was used. The flow-rate was 1.0 ml/min, and the volume of the injected polymer solution was always 2 ml corresponding to the total loop volume.

The benzene and methanol solvents were purified and dried in the usual way. The polymer solutions were prepared immediately before injection using solvent mixtures from the solvent reservoir. The poly(dimethylsiloxane) test polymer was a commercial sample from Rhone Poulenc (Paris, France). From light scattering, $\bar{M}_w = 62,000$ and from independent GPC measurements, the polydispersity ratio, $(\bar{M}_w/\bar{M}_n) = 1.3$. The two atactic poly(methyl methacrylate) samples had molecular weights ($\bar{M}_w$) of 210,000 and 550,000 from light scattering.

RESULTS AND DISCUSSION

The system benzene (1)–methanol (2)–poly(dimethylsiloxane) (3)

In Fig. 1 are shown the chromatograms of poly(dimethylsiloxane), PDMS, at different polymer concentrations in benzene–methanol (90:10). Two negative peaks corresponding to solvated polymer ($V_e = V_0 = 72.0$ ml) and to non-adsorbed
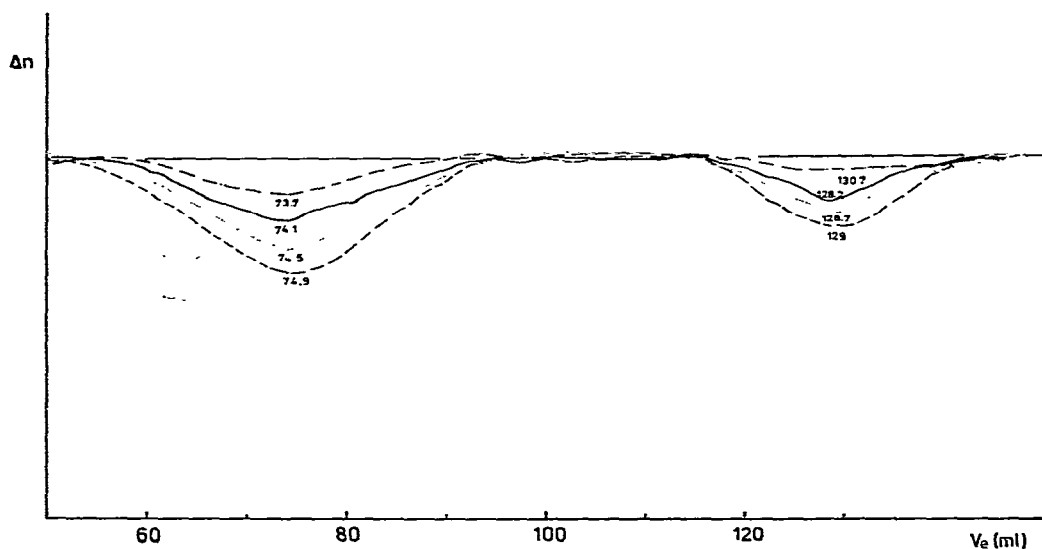

Fig. 1. Chromatograms of PDMS ($\bar{M}_w = 62,000$) in a benzene–methanol mixture (90:10), at different polymer concentrations: —·—, 2.01; ———, 4.36; · · ·, 5.03 and — —, 6.25 mg/ml.
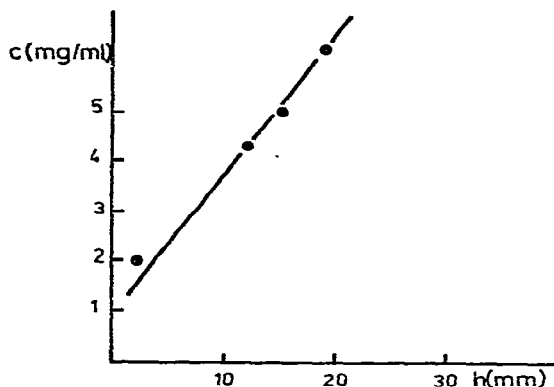
Fig. 2. Dependence of the height of the vacant peak on PDMS concentration in benzene–methanol (90:10).

methanol ($128.2 < V_e < 130.7$ ml) are seen. As shown in Fig. 2, the heights of the vacant peaks are proportional to the amount of injected polymer. This indicates that the polymer is preferentially solvated by benzene[10].

PDMS chromatograms obtained at several eluent compositions are shown in Fig. 3. Even taking into account the differences in polymer concentration of the injected solutions (see Table I), it can be seen that the size of the polymer peak decreases with increasing amount of methanol in the mixture. This behaviour could be expected since the refractive index of the mixture approaches that of the polymer on increasing the methanol concentration. The vacant peak, however, follows the opposite trend, i.e., it increases with increasing methanol content. This means that
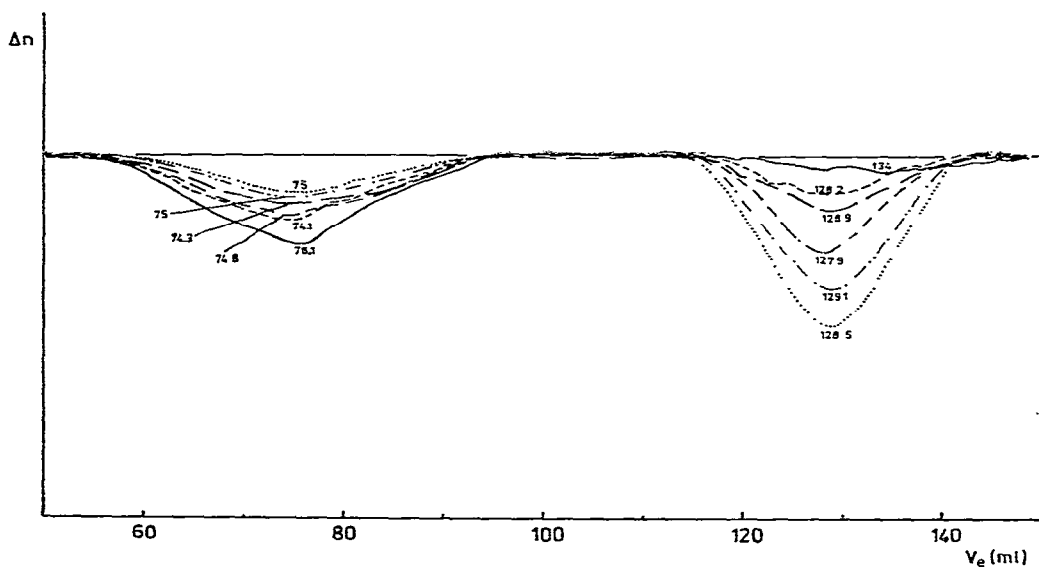

Fig. 3. Chromatograms of PDMS in different benzene–methanol mixtures. v_2: ———, 0.05; – – –, 0.10; — — —, 0.13; – · – ·, 0.16; – · · — · ·, 0.20; · · ·, 0.25.

the preferential solvation of the polymer by benzene increases with increasing amount of the methanol in the mixture.

From the above considerations, the way in which preferential solvation takes place, and its dependence on mixture composition, can be easily visualized. The next step is to relate, in a quantitative form, the size of the vacant peak to the parameter λ, which is usually employed to evaluate the prefential solvation phenomenon. When a solvent (1) is preferentially adsorbed by a polymer in a ternary system solvent (1)–solvent (2)–polymer (3), λ can be defined as the change in volume fraction of component 1 with respect to the polymer concentration in the dialyzed solvent at infinite dilution. The expression for λ would be:

$$\lambda = \frac{dv_1}{dc_3} = -\frac{dv_2}{dc_3} \tag{1}$$

Keeping in mind the above formula, the following experimental procedure was followed for the determination of λ.

Before injecting any polymer, a methanol solution of known concentration in a given solvent mixture was injected. The difference in the volume fraction of benzene between the above solution and the mixture, Δv_1^0, was related to the height of the methanol peak, h_1. Subsequent injection of polymer solution will cause a vacant methanol peak, height h_2, which can be related to the change in the volume fraction of benzene, Δv_1, due to its preferential adsorption:

$$\Delta v_1 = \Delta v_1^0 \cdot \frac{h_2}{h_1} \tag{2}$$

Replacing the differentials in eqn. 1 by increments and substituting into eqn. 1 the Δv_1 value given by eqn. 2, λ may be expressed as:

$$\lambda = \frac{\Delta v_1^0}{c_3} \cdot \frac{h_2}{h_1} \tag{3}$$

The results of the different chromatograms performed for the system benzene (1)–methanol (2)–PDMS (3) are in Table I: v_1 is the mole fraction of benzene; c_2 is the concentration of methanol injected resulting in a peak of height h_1, corresponding to a change Δv_1^0 in the volume fraction of benzene; c_3 is the polymer concentration in g/ml resulting in a vacant methanol peak of height h_2 and elution volume V_e. The λ values were calculated from eqn. 3. The elution volumes corresponding to the vacant peaks in the different mixtures ranged from 128.0 to 129.0 ml, except for the mixture having the lowest methanol content for which the elution volume of the vacant peak appeared at 134.0 ml. As Fig. 3 shows, this effect may be due to retention of methanol by the chromatographic support. Static differential refractometry measurements performed independently support this hypothesis. Effectively, after a short equilibration time of *ca.* 2 h, methanol is preferentially adsorbed by the Spherosil. Although the amount of methanol adsorbed remains constant independent of the methanol content in the mixture, mixtures containing small amounts of methanol will exhibit higher relative retentions those containing larger amounts.

TABLE I

DETERMINATION OF THE PREFERENTIAL SOLVATION PARAMETER λ FOR THE SYSTEM BENZENE (1)–METHANOL (2) –PDMS (3) ($\bar{M}_w$ = 62000) FROM GEL PERMEATION CHROMATOGRAMS AT DIFFERENT MIXTURE COMPOSITIONS

v_1	c_2 (ml/100 ml)	$\Delta v_1^0 \cdot 10^3$	c_3 (mg/ml)	h_1 (mm)	h_2 (mm)	V_e (ml)	λ (ml/g)
0.95	0.231	2.19	5.07	54 ± 1	4 ± 2	134.0	0.03 ± 0.02
0.90	0.242	2.18	4.36	50 ± 1	10 ± 1	128.2	0.10 ± 0.01
0.87	0.245	2.13	3.93	49 ± 1	14 ± 2	128.9	0.16 ± 0.03
0.84	0.240	2.02	5.29	47 ± 1	26 ± 1	127.9	0.21 ± 0.01
0.80	0.251	2.01	6.24	42 ± 1	36 ± 1	129.1	0.28 ± 0.01
0.75	0.248	1.86	6.80	37 ± 1	46 ± 2	128.5	0.34 ± 0.02

This peak broadening effect at low methanol compositions hampers the estimation of the heights of the vacant peaks with the result that the calculated λ values may suffer higher relative errors.

Fig. 4 shows a plot of the calculated values of λ versus v_2, together with the results of Hert and Strazielle[4] from light scattering and differential refractometry after dialysis equilibrium. The small difference in molecular weight between the earlier sample and ours (58,000 and 62,000, respectively) will hardly be reflected in the λ values. The agreement between the two sets of λ values is remarkable. Moreover, the GPC technique is not limited by the composition of the mixture as occurs with light scattering. In the ternary system studied, it is not possible to determine λ by light scattering, for mixtures of composition $v_2 > 0.13$, as pointed out by Hert and Strazielle[4].
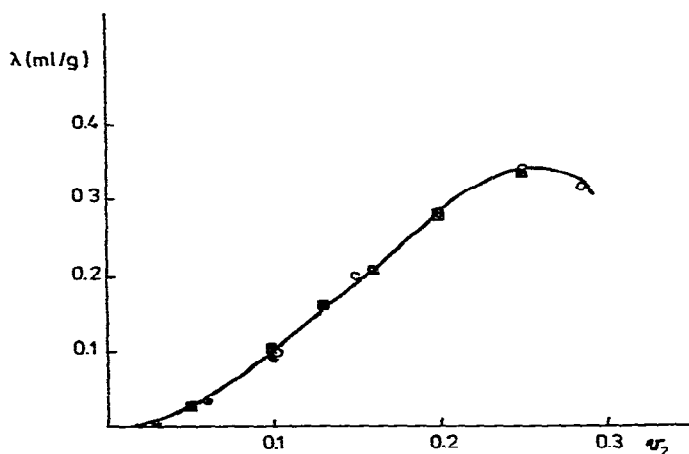

Fig. 4. Dependence of the parameter λ on mixture composition for the system benzene–methanol–PDMS. (■) GPC values; (○) values from refractometry after dialysis[4]; (●) values from light scattering[4].

The system benzene(1)–methanol(2)–poly(methyl methacrylate) (3)

In Fig. 5a are shown the chromatograms of poly(methyl methacrylate), PMM ($\bar{M}_w$ = 550,000), at three different polymer concentrations in benzene–methanol

(70:30). Fig. 5b provides evidence for the preferential solvation phenomenon. Chromatograms of the two PMM polymers with $\bar{M}_w = 210,000$ and $550,000$, respectively, are shown at several mixture compositions in Figs. 6 and 7. It can be seen that the elution volumes for both polymers are similar. This is due to the fact that both polymers fall outside the effective separation range of the Spherosil column used. Since we are interested only in the vacant peaks the above fact is unimportant.
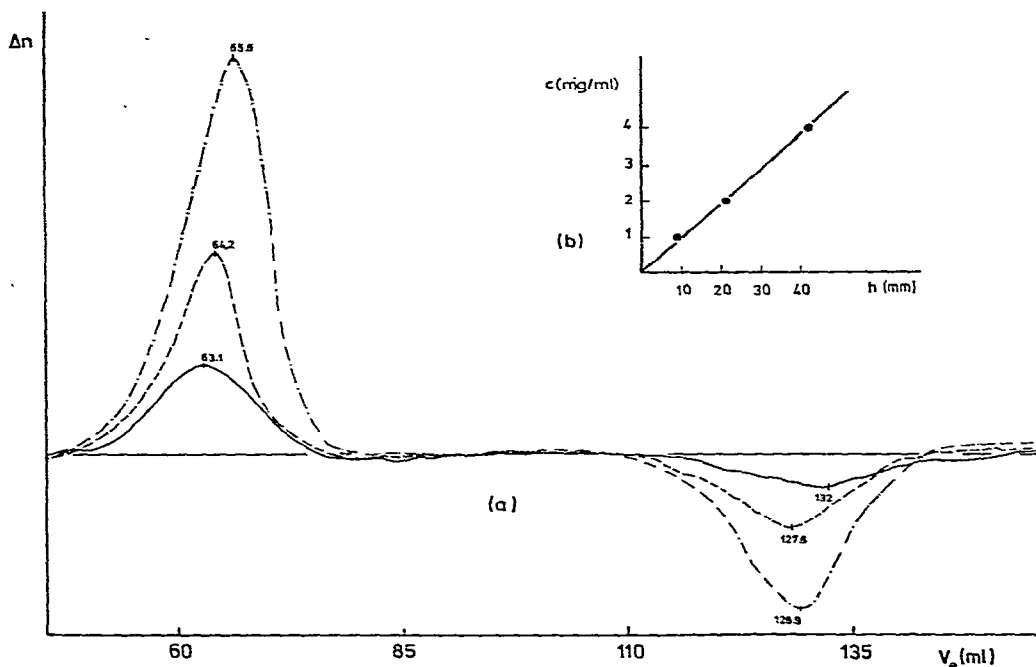

Fig. 5. (a) Chromatograms of PMM ($\bar{M}_w = 550,000$) in a benzene–methanol mixture (70:30), at different concentrations: ————, 1.03; – – –, 0.202; – · –, 0.402 mg/ml. (b) Dependence of the size of the vacant peak on PMM concentration.

All the chromatograms in Figs. 6 and 7 show the corresponding vacant peaks. Positive peaks due to benzene appear in mixtures of low methanol content. In these cases, methanol is preferentially adsorbent by the polymer. On the other hand, negative peaks appear in methanol-rich mixtures and in these cases benzene is preferentially adsorbed. The analysis of this inversion phenomenon indicates that it takes place at $0.16 < v_2 < 0.17$, in accordance with published results determined by classical techniques[11]. The elution volumes of the vacant benzene peaks are coincident with the elution volume of the peak obtained by benzene injection. This is not the case for the vacant methanol peaks. Their elution volumes and sizes follow the same trends as in the benzene–methanol–PMDS system discussed above.

Table II collects the chromatographic parameters and the λ values calculated from eqn. 3. The λ values are plotted versus v_2 in Fig. 8. The solid line in Fig. 8 represents λ data determined from dialysis equilibrium by Pouchly et al.[11]. Unfortunately, since these workers did not indicate the molecular weight of the polymer studied, it is not possible to make any comparisons. Measurements of λ by dialysis equilibrium
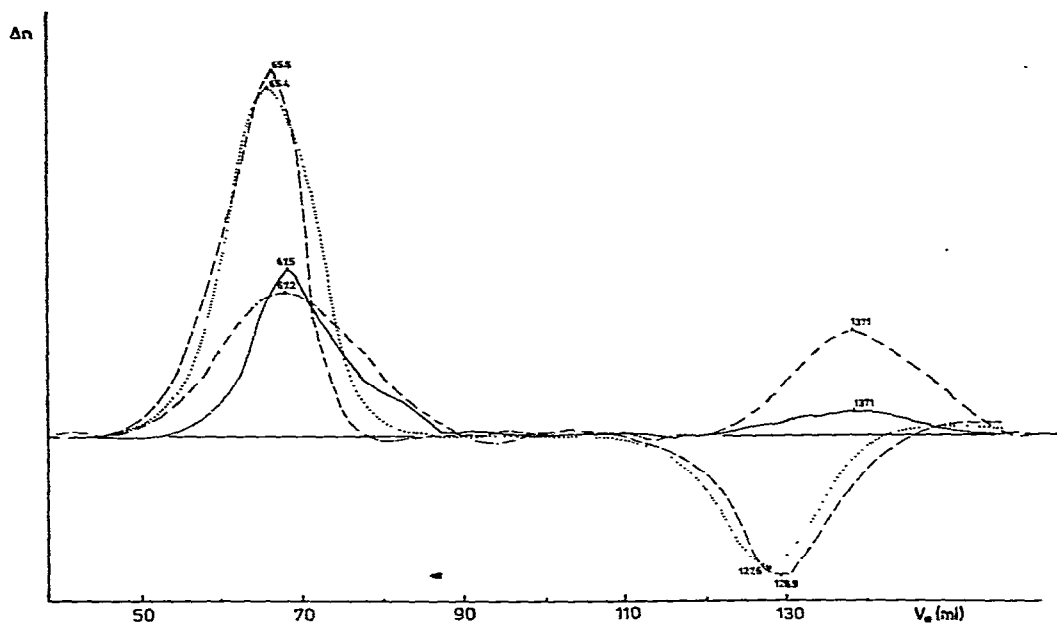
Fig. 6. Chromatograms of PMM ($\bar{M}_w = 210,000$) in different benzene–methanol mixtures. v_2: — · — ·, 0.08; ——, 0.17; — — —, 0.30; · · ·, 0.40.
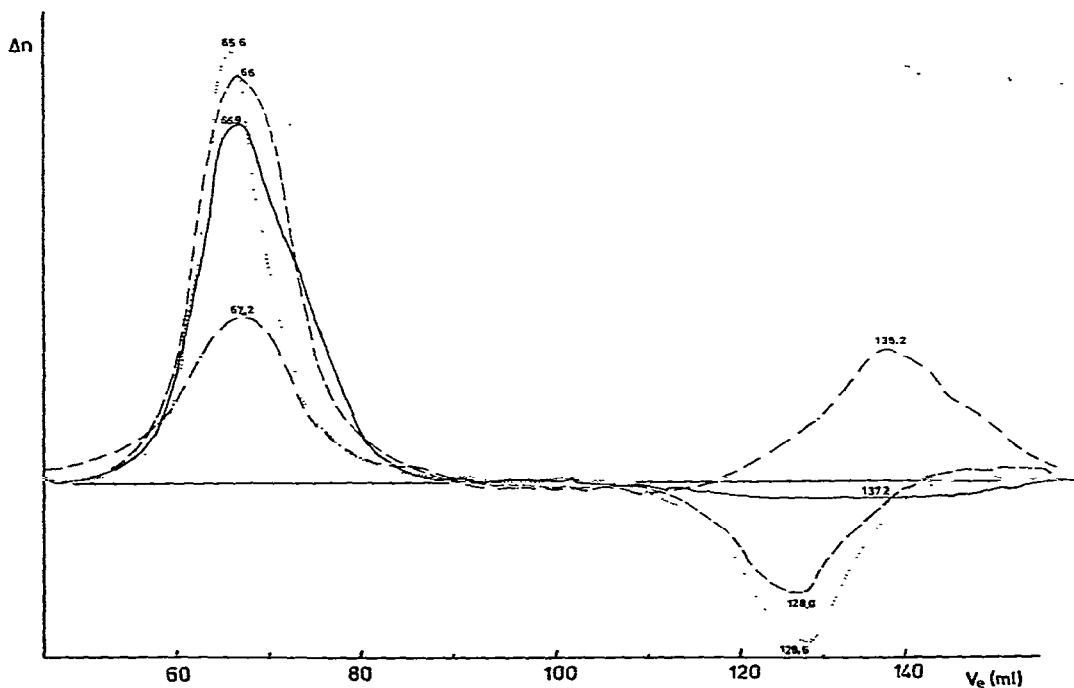

Fig. 7. Chromatograms of PMM ($\bar{M}_w = 550,000$) in different benzene–methanol mixtures. v_2: — · — ·, 0.08; ——, 0.16; — — —, 0.30; · · ·, 0.40.

TABLE II

DETERMINATION OF THE PREFERENTIAL SOLVATION PARAMETER λ FOR THE SYSTEMS BENZENE (1) – METHANOL (2) – PMM (3) ($\bar{M}_w$ = 210000 AND 550000) FROM GEL PERMEATION CHROMATOGRAMS AT DIFFERENT MIXTURE COMPOSITIONS

Sample	v_1	c_2 (ml/100 ml)	$\Delta v_1^0 \cdot 10^3$	c_3 (mg/ml)	h_1 (mm)	h_2 (mm)	V_e (ml)	λ (ml/g)
PMM 210,000	0.92	1.901 *	1.52	14.99	11 ± 1	36 ± 2	138.2	−0.33 ± 0.06
PMM 550,000	0.92	1.901 *	1.52	15.02	11 ± 1	30 ± 2	137.1	−0.28 ± 0.06
PMM 210,000 **	0.83	0.261	2.17	6.01	46 ± 1	5 ± 1	137.2	0.009 ± 0.002
PMM 550,000	0.84	1.571 *	2.51	6.01	22 ± 1	6 ± 1	137.1	−0.11 ± 0.01
PMM 210,000	0.70	0.275	1.93	4.00	64 ± 1	32 ± 3	128.0	0.24 ± 0.03
PMM 550,000	0.70	0.275	1.93	4.02	64 ± 1	42 ± 4	128.9	0.31 ± 0.04
PMM 210,000	0.60	0.283	1.70	3.98	52 ± 1	45 ± 1	128.6	0.37 ± 0.02
PMM 550,000	0.60	0.283	1.70	4.00	52 ± 1	40 ± 1	127.6	0.33 ± 0.02

* The pure component injected was benzene, so the numbers are really c_1 values.
** The h_1 and h_2 values were determined at half and double the sensitivity with respect to the rest of the chromatograms.

were therefore made for these systems ($\bar{M}_w$ = 220,000 and 550,000) in this laboratory. The results are also shown in Fig. 8.

It can be seen that the results of the GPC and dialysis equilibrium measurements differ for negative values of λ. A plausible explanation for this may be as follows. When the polar methanol is preferentially adsorbed by PMM, notable adsorption and retention phenomena may take place between the polymer solvated by methanol and the Spherosil support. As a result, the amount of methanol surrounding the polymer may increase with respect to that of the thermodynamic equilibrium and
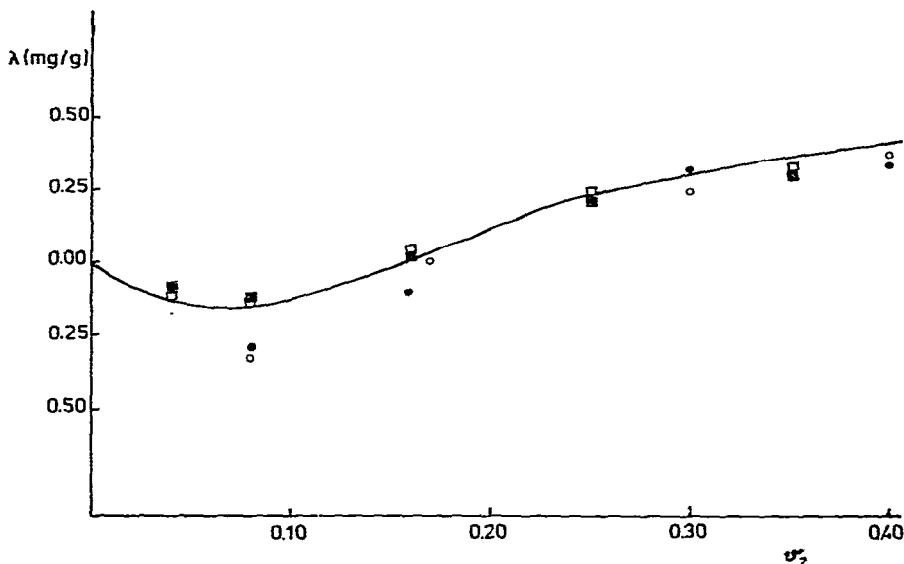

Fig. 8. Dependence of the parameter λ on mixture composition for the system benzene–methanol–PMM. (O) and (●) GPC values; (□) and (■) values from refractometry after dialysis. Open symbols for $\bar{M}_w$ = 210,000, filled symbols for $\bar{M}_w$ = 550,000. Solid line, dialysis equilibrium values[11].

the size of the benzene peak, and hence the absolute values of λ, will increase. A possible way of correcting the low negative λ values obtained by GPC may be by the use of a chromatographic support having larger diameter pores. Exploratory differential refractometry experiments have shown that the adsorption of polar solvents by Spherosil decreases with increasing pore size.

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