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by

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Volume Changes With Mole Fraction For Two And Three Component Systems

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SUMMARY

The rate of polymerization is determined by measuring the volume contraction in dilatometer and from the knowledge of the densities of the monomer and polymer. The method is based on assuming ideal mixing of both the monomer and polymer with the solvent used.

In this work, this assumption was tested experimentally in the cases of methyl acrylate-acetone, Polymethyl acrylate-methyl acrylate, polymethyl acrylate-acetone, polymethyl acrylate-methyl acrylate-acetone and methyl acrylate-carbon tetrachloride systems.

Introduction

The volume change observed in polymerization reaction has been used extensively as a mean of calculating the percentage of conversion of monomer to polymer. Various design of dilatometers for the purpose of measuring this volume change have been used and these practical arrangements have been discussed. The calculation of the percentage conversion from the observed volume change is generally quite simple, provided that the densities of the monomer and polymer are known. Neither of these two quantities present any difficulties, provided that the mixing of monomer, polymer and solvent involves no volume change.

General treatment of calculating the percentage conversion at any time t in the polymerization carried out in dilatometer is as follows:

$$V_t = V_{sol.} + V_{mon.} + V_{pol.} \quad (1)$$

$$V_t = n_1 V_1 + n_2 V_2 + n_3 V_3 \quad (2)$$

where n_1, n_2, n_3 are the numbers of moles and V_1, V_2, V_3 are the partial molar volumes of the components. If the mixture is ideal then partial molar volumes are the same as the molar volumes of the pure components.

$$V_t = n_1 V^\circ_1 + n_2 V^\circ_2 + n_3 V^\circ_3 \quad (3)$$

$$V_t = n_1 \frac{M_1}{d_1} + n_2 \frac{M_2}{d_2} + n_3 \frac{M_3}{d_3} \quad (4)$$

or

$$V_t = \frac{W_1}{d_1} + \frac{W_2}{d_2} + \frac{W_3}{d_3} \quad (5)$$

In the reaction mixture at any time t,

$$W_2 + W_3 = W_0$$

and

$$V_t = \frac{W_1}{d_1} + \frac{W_2}{d_2} + \frac{W_0 - W_2}{d_3} \quad (6)$$

Since no polymer is present at the begining of the polymerization, equation (6) takes the form,

$$V_0 = \frac{W_1}{d_1} + \frac{W_0}{d_2} \quad (7)$$

Volume change at the time t is deduced from equation (7) and (6), as follows:

$$\Delta V = V_t - V_0$$

$$\Delta V = W_3 \left(\frac{1}{d_2} - \frac{1}{d_3}\right) \quad (8)$$

But considering the situation at infinit time then

$$W_3 = W_0$$

$$\Delta V_{\infty} = W_0 \left(\frac{1}{d_2} - \frac{1}{d_3}\right) \tag{9}$$

and from equations (9) and (8) the fractional conversion could be found as follows:

$$\frac{\Delta V}{\Delta V_{\infty}} = \frac{W_3}{W_0} \tag{10}$$

In addition polymerization reactions, where no termination processe takes place, the average molecular weight of the polymer in the reaction mixture increases with time. In general, the densities of a series of polymers increase as the molecular weights increase. So, in the case under discussion, it might be thought that the calculation of the percentage conversion from the volume. change, would require a knowledge of the particular density appropriate to the polymer formed at each particular stage. It has been already shown that this view is not correct (1).

A much more serious problem in dilatometry arises when the components of the reaction mixture mix together with a change in volume. This point has been emphasized by Treloar (2) who pointed out that the volume change could be much reduced by appropriate choice of solvent.

Treloar measured the density of solutions of styrene and polystyrene in two solvents, carbon tetrachloride and 1,2-dichloroethane. For either the monomer or the polymer alone, the density of the solution in carbon tetrachloride or 1,2-dichloroethane was a linear function of the concentration. The density of the solution containing the same total concentration of (styrene + polystrene) and 1,2-dichloroethane was also a linear function of the concentration. In these case the assumption that percentage conversion is proportional to density and hence, volume contraction is clearly true. However, in carbon tetrachloride solution, there existed a marked deviation from ideal behaviour and this was most pronounced when the ratio of polymer to monomer was low, which are the most important from the kinetic point of view, so it will be quite useful to know the behaviour of the polymer solutions in the kinetic treatement.

Let us take a three compenent system which has the weight fractions W_1, W_2 and W_3 from the solvent, monomer and polymer respectively.

If the solution is an ideal mixture then no volume change will be observed.

$$\frac{100}{d_s} = \frac{W_1}{d_1} + \frac{W_2}{d_2} + \frac{W_3}{d_3}$$

In this work this view has been tested experimentally by measuring solution densities having two and three components.

Experimental

Polymethyl acrylate was prepared by the method described in the reference (3). Density of the pure solvents and the solutions were measured at 25°C in a 25 ml pyknometer having two capillaries. The density of the polymethyl acrylate was measured in a density gradient column constructed at 25°C.

Construction of the Column

Density gradient column was constructed according to the "Slip-Under" method. The apparatus used for this method is given in the reference (4). In this experiment the column was prepared with 24.7463 % and 20.5523 % of sodium sulphate solution (5).

In this experiment the top and bottom density of the column were 1.19475 g cc^{-1} and 1.23325 g cc^{-1}. Densities of the three glass floats prepared to calibrate density gradient column were measured by floatation method as 1.2092 g cc^{-1}, 1.2204 g cc^{-1}, 1.2228 g cc^{-1}. The length of the column was 55 cm.

Measurement of the Density of the Polymer Sample

A polymer film was prepared on the hot plate and two air bubble free samples were taken from it, and gently were put in the column. Their levels have been determined with a cathetometer. Density of the polymer samples were calculated from the density of the second glass float closer to the polymer samples. The experimental results are tabulated in Table I.

TABLE I

Experimental Results for Density Measurements of Polymethl Acrylate
($d_0 = 1.19475$ g cc^{-1}, $d_l = 1.23325$ g cc^{-1}, $l = 55$ cm.)

Glass floats	Density of Glass floats (g cc^{-1})	Level of the Glass Floats (cm)	Density increment (g cm^{-1})
1	1.2092 g cc^{-1}	35.50	7.4×10^{-4}
2	1.2204 g cc^{-1}	20.32	7.2×10^{-4}
3	1.2228 g cc^{-1}	16.97	7.0×10^{-4}

Polymer Samples	Level of the Polymer Sample (cm)	Density of the Polymer (g cc^{-1})
1	23.71	1.2180
2	23.43	1.2182

The results of the pyknometer measurements of two and three components systems are tabulated in the following tables.

TABLE II–a

Compositions of the Mixtures of Methyl Acrylate (1) and Acetone (2)
($d_1 = 0.94855$ g cc^{-1}, $d_2 = 0.78489$ g cc^{-1}, at 25°C)

Soln.	W_1	W_2	n_1	n_2	n	X_1	X_2
1	26.5151	73.4849	0.3080	1.2652	1.5732	0.1958	0.8042
2	50.3320	49.8641	0.5846	0.8551	1.4397	0.4061	0.5939
3	63.4383	36.5617	0.7369	0.6295	1.3664	0.5393	0.4607
4	77.3056	22.6944	0.8979	0.3907	1.2886	0.6968	0.3032
5	90.3965	9.6035	1.0500	0.1653	1.2153	0.8640	0.1360

TABLE II–b

Pyknometer Results and Volume Changes in the Myhyl Acrylate - Aceton Systems.

Soln.	d_s	V_1	V_2	V_s	ΔV	ΔV mole^{-1}
1	0.82273	27.953	93.624	121.546	—0.031	—0.0197
2	0.85986	53.062	63.280	116.298	—0.044	—0.0306
3	0.88180	66.876	46.582	113.404	—0.054	—0.0395
4	0.90600	81.499	28.914	110.375	—0.038	—0.0295
5	0.93011	95.296	12.235	107.514	—0.017	—0.0140

TABLE III–a

Compositions of the Mixtures of Polymethyl Acrylate (1) and Methyl Acrylate (2) ($d_1 = 1.21815$ g cc^{-1}, $d_2 = 0.94855$ g cc^{-1} at 25°C)

Soln.	W_1	W_2	n_1	n_2	n	X_1	X_2
1	1.1397	98.8603	0.0132	1.1484	1.1616	0.0114	0.9886
2	3.1840	96.8160	0.0370	1.1246	1.1616	0.0319	0.9681
3	4.5944	95.4056	0.0534	1.1082	1.1616	0.0456	0.9544

TABLE III–b

Pyknomoter Results and Volume Changes in the Polymethyl Acrylate (1) - Methyl Acrylate (2) Systems

Soln.	d_s	V_1	V_2	V_s	ΔV	ΔV mole^{-1}
1	0.95114	0.936	104.223	105.137	—0.022	—0.0189
2	0.95579	2.614	102.067	104.625	—0.056	—0.0482
3	0.95896	3.772	100.580	104.280	—0.072	—0.0620

TABLE IV–a

Compositions of the Mixtures of Polymethyl Acrylate (1) and Acetone (2) ($d_1 = 1.21815$ g cc^{-1}, $d_2 = 0.78489$ g cc^{-1} at 25°C)

Soln.	W_1	W_2	n_1	n_2	n	X_1	X_2
1	1.2335	98.7665	0.0143	1.7005	1.7148	0.0083	0.9917
2	2.7530	97.2470	0.0320	1.6743	1.7063	0.0188	0.9812
3	4.2274	95.7726	0.0491	1.6489	1.6980	0.0289	0.9711

TABLE IV–b

Pyknometer Results and Volume Changes in the Polymethyl Acrylate (1) - Acetone (2) Systems

Soln.	d_s	V_1	V_2	V_s	ΔV	ΔV (mole^{-1})
1	0.78864	1.013	125.835	126.801	—0.047	—0.0268
2	0.79310	2.260	123.889	126.088	—0.071	—0.0416
3	0.79735	3.470	122.021	125.415	—0.076	—0.0448

TABELA V-a

Compositions of the Mixtures of Polymethyl Acrylate (1), Methyl Acrylate (2) and Acetone (3)

($d_1 = 1.21815$ g cc^{-1}, $d_2 = 0.94855$ g cc^{-1}, $d_3 = 0.78489$ g cc^{-1} at 25°C)

	W_1	W_2	W_3	n_1	n_2	n_3	n	X_1	X_2	X_3
1	1.0746	45.1555	53.7699	0.0125	0.5245	0.9258	1.4628	0.0085	0.3686	0.6229
2	4.9203	44.8727	50.2070	0.0572	0.5212	0.8644	1.4428	0.0396	0.3612	0.5992

TABLE V-b

Pyknometer Results and VolumeChanges in the Polymethyl Acrylate (1)-Methyl Acrylate (2) Acetone (3) Systems

Soln.	d_s	V_1	V_2	V_3	V_s	ΔV	ΔV ($mole^{-1}$)
1	0.85529	0.882	47.605	68.506	116.919	—0.074	—0.0506
2	0.86828	4.039	47.307	63.967	115.176	—0.143	—0.0991

TABLE VI-a

Compositions of the Mixtures of Methyl Acrylate (1) and Carbon Tetrachloride (2)
($d_1 = 0.94860$ g cc^{-1}, $d_2 = 1.58411$ g cc^{-1} at 25°C)

Exp. I Soln.	W_1	W_2	n_1	n_2	n	X_1	X_2
1	77.7332	22.2668	0.9029	0.1447	1.0476	0.8619	0.1381
2	59.0474	40.9526	0.6859	0.2662	0.9521	0.7204	0.2796
3	39.9989	60.0011	0.4646	0.3900	0.8546	0.5436	0.4564
4	19.5208	80.4792	0.2267	0.5231	0.7498	0.3023	0.6977

($d_1 = 0.94858$ g cc^{-1}, $d_2 = 1.58416$ g cc^{-1} at 25°C)

Exp. II Soln.	W_1	W_2	n_1	n_2	n	X_1	X_2
1	79.8504	20.1496	0.4818	0.1310	0.9728	0.8653	0.1347
2	38.4525	61.5475	0.4466	0.4001	0.8467	0.5275	0.4725
3	27.4941	72.5059	0.3194	0.4713	0.7907	0.4039	0.5961
4	17.7081	82.2919	0.2057	0.5349	0.7406	0.2777	0.7223
5	9.3295	90.6705	0.1084	0.5894	0.69.8	0.1553	0.8447

TABLE VI-b

Pyknometer Results and Volume Changes in the Methyl Acrylate (1) - Carbon Tetrachloride (2) Systems

exp. I Soln.	d_s	V_1	V_2	V_s	ΔV	ΔV (mole^{-1})
1	1.04050	81.947	14.055	96.108	0.106	0.1021
2	1.13299	62.247	25.852	88.262	0.163	0.1712
3	1.24644	42.166	37.877	80.228	0.185	0.2165
4	1.39797	20.579	50.804	71.532	0.149	0.1987

($d_1 = 0.94858$ g cc^{-1}, $d_2 = 1.58416$ g cc^{-1} at 25°C)

Exp. II Soln.	sd_s	V_1	V_2	V_s	ΔV	ΔV (mole^{-1})
1	1.03098	84.179	12.719	96.995	0.097	0.0997
2	1.25682	40.537	38.852	79.566	0.177	0.2090
3	1.33459	28.984	45.769	74.929	0.176	0.2226
4	1.41323	18.668	51.947	70.760	0.145	0.1958
5	1.48877	9.835	57.236	67.169	0.098	0.1404

Conclusion

The magnitude of the deviation from ideal behaviour for both polymethyl acrylate - acetone and polymethyl acrylate-methyl acrylate is the same within the range of experimental error. In the case of methyl acrylate - carbon tetrachloride volume change due to non-ideality is in opposite sign. By comparision of the two curves in Figure 2, it is obvious that the deviation from ideality in carbon tetrachloride is much more pronounced than that in acetone. Secondly the volume change is opposite in sign. Methyl acrylate dissolves in polar solvent such as acetone with little volume change, but dissolvos in non-polar solvent, such as carbon tetrachloride, with biger volume change.

The experimental result obtained from this work is that during the polymerization of methyl acrylate alone (bulk polymerization) or in acetone volume of the solution in dilatometer decreases not only due to the conversion of monomer to polymer but also due to dissolution of the two components.

On the other hand, in case of the polymerization of methyl acrylate in carbon tetrachloride two opposite volume changes must be considered, first volume decreases due to polymerization, secondly volume increases as the result of dissolution of the two components. So volume change observed in dilatometer will be

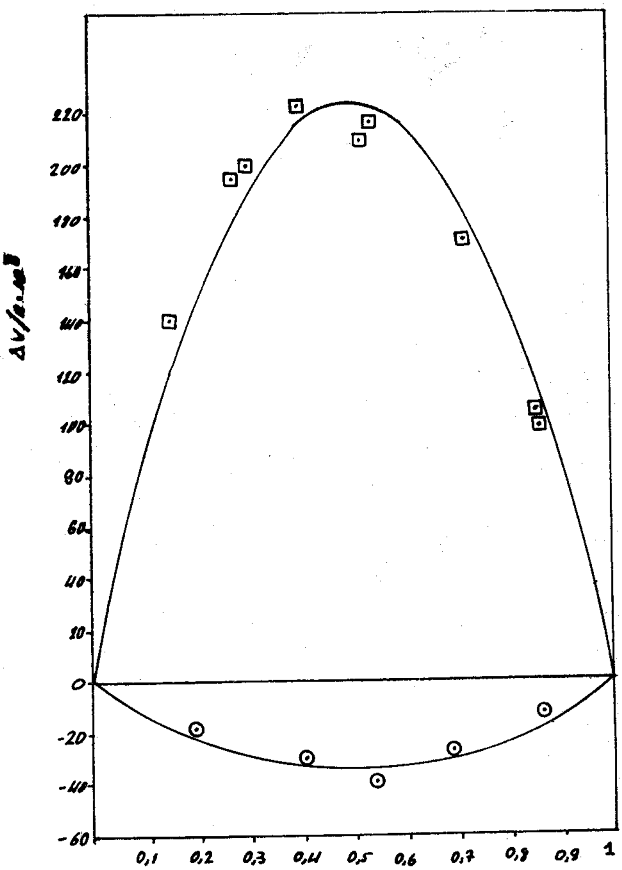

Figure 2. Methyl acrylate-Corbon Tetrachloride, ⊡ Methyl acrylate-Acetone, ⊙

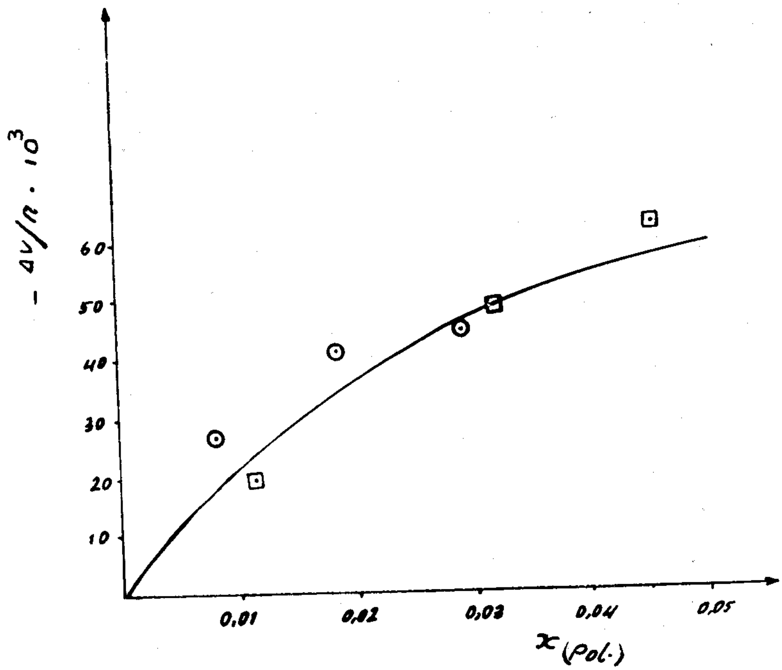

Figure 3. Polymethyl acrylate-Acetone, ⊙ Poiymethyl acrylats-Methyl acrylate, ⊡

less than the true volume change. Consequently polymerization percentage or rate of polymerization calculated from this observed volume change will be less than the true value. So it is suggested that when dilatometry is used to determine polymerization percentage or rate of polymerization, the behaviour of the solution must be taken into account in case of bulk or solution polymerization of methyl acrylate.

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Ö Z E T

Polimerizasyon hızı dilatometrede gözlenen hacim küçülmesi ve monomer ile polimerin yoğunlukları ölçülerek tayin edilir. Bu yöntem polimer, monomer ve çözücünün ideal bir karışım meydana getirdiği kabulüne dayanır.

Bu çalışmada metil akrilat-aseton, polimetil akrilat-metil akrilat, polimetil akrilat-aseton, polimetil akrilat-metil akrilat-aseton, ve metil akrilat-karbon tetra kloürür sistemlerinde hacim değişmeleri incelenmiştir.

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