

Thermodynamic Studies of Polyvinyl Acetate Solutions in the Dilute and Moderately Concentrated Range

George V. Browning and John D. Ferry

Citation: *The Journal of Chemical Physics* **17**, 1107 (1949); doi: 10.1063/1.1747122

View online: <http://dx.doi.org/10.1063/1.1747122>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/17/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

Short-range order and collective dynamics of poly(vinyl acetate): A combined study by neutron scattering and molecular dynamics simulations

J. Chem. Phys. **129**, 224903 (2008); 10.1063/1.3028210

Concentration Dependence of Rheology for Poly(vinyl Acetate) Solutions

J. Rheol. **25**, 171 (1981); 10.1122/1.549643

Theory of Moderately Concentrated Polymer Solutions

J. Chem. Phys. **43**, 1334 (1965); 10.1063/1.1696924

Dielectric Studies of the Polymer Polyvinyl Acetate in the Molten State

J. Chem. Phys. **36**, 2523 (1962); 10.1063/1.1732924

Mechanical Properties of Substances of High Molecular Weight. VIII. Dispersion of Dynamic Rigidity and Viscosity in Concentrated Polyvinyl Acetate Solutions

J. Appl. Phys. **21**, 513 (1950); 10.1063/1.1699696



Thermodynamic Studies of Polyvinyl Acetate Solutions in the Dilute and Moderately Concentrated Range

GEORGE V. BROWNING AND JOHN D. FERRY

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

(Received April 1, 1949)

Osmotic pressure measurements on polyvinyl acetate solutions have provided values of the constant μ in methyl ethyl ketone, 1,2,3-trichloropropane, acetone, dioxane, and dimethyl phthalate. Modifications in techniques have permitted measurements in the first two solvents at different temperatures at concentrations (c) up to 0.07 g/cc. The osmotic pressure can be expressed as a power series in c with three terms; the coefficients of c^2 and c^3 are larger in trichloropropane than in methyl ethyl ketone. The partial molal heats, entropies, and free energies of dilution in these two solvents have been calculated. All are numerically greater for trichloropropane. The heats of dilution are negative; $\Delta\bar{H}_1/v_2^2$ is roughly constant for methyl ethyl ketone but increases somewhat with concentration for trichloropropane. The entropies of dilution are much smaller than those given by the lattice theory.

THE steady flow viscosity and other mechanical properties of polyvinyl acetate solutions show a considerable dependence on the choice of solvent, which may be attributed in part to differences in specific polymer-solvent interaction. The thermodynamic properties also differ, and can provide some information concerning the magnitude of the interactions.

Most thermodynamic data from osmotic pressure measurements on polymer solutions have been limited to the range of very dilute solutions; exceptions are found in the work of Gee and Meyer¹ on rubber and Schick on polystyrene.² In the present study, we have extended osmotic pressure measurements on polyvinyl acetate over the concentration range up to about 0.07 g/cc. Data for solutions in methyl ethyl ketone and in 1,2,3-trichloropropane at different temperatures are reported here, together with a few measurements in several other solvents and some comments on experimental techniques. Our systems differ from others which have been investigated in the range of higher concentrations in that both polymer and solvents are polar.

MATERIALS

Polyvinyl acetate AYAX, lot 1232, was obtained through the kindness of Mr. A. K. Doolittle of Carbide and Carbon Chemicals Corporation. The whole polymer was used for some measurements, but it contained material of very low molecular weight which diffused through the osmotic membranes in certain solvents. Accordingly, to obtain samples with a somewhat sharper distribution of molecular weight, a rough fractionation was performed.³ The solvent was acetone and the precipitant a mixture of equal volumes of water and methyl alcohol. Three fractions were separated; they were dissolved in benzene and dried from frozen solutions. Their relative amounts, number-average molecular weights,

and intrinsic viscosities in methyl ethyl ketone at 25° are given in Table I, together with the values of k' in the equation⁴ $\eta_{sp}/c = [\eta] + k'[\eta]^2c$. The fractions comprised 85 percent of the initial sample, the remaining 15 percent representing principally material of very low molecular weight.

Density measurements⁵ on solutions of the whole polymer over the concentration range up to 10 percent in methyl ethyl ketone and to 5 percent in trichloropropane, at 13° and 40°C, showed that in each case the specific volume of the solution (\bar{v}) was a linear function of the weight fraction of polymer (w_2), as represented by the following equations:

in methyl ethyl ketone

$$\begin{aligned} \text{at } 13^\circ, \bar{v} &= 1.232 - 0.411w_2; \bar{v}_2 = 0.821 \\ \text{at } 40^\circ, \bar{v} &= 1.275 - 0.442w_2; \bar{v}_2 = 0.833, \end{aligned}$$

in 1,2,3-trichloropropane

$$\begin{aligned} \text{at } 13^\circ, \bar{v} &= 0.7161 + 0.114w_2; \bar{v}_2 = 0.830 \\ \text{at } 40^\circ, \bar{v} &= 0.7346 + 0.106w_2; \bar{v}_2 = 0.841. \end{aligned}$$

Linear interpolation was used to obtain values at other temperatures. In the case of methyl ethyl ketone, the specific volume and its temperature dependence agreed with the data of Doty and Mishuck.⁶ According to the linear dependence on w_2 , the partial specific volume of solvent was at all concentrations equal to the specific

TABLE I. Polyvinyl acetate fractions.

No.	Relative amount, percent	\bar{M}_n	$[\eta]^a$	k'
Unfractionated	100	140,000	0.96	0.37
I	13	840,000	1.61	0.48
II	56	280,000	0.98	0.46
III	16	62,000	0.34	1.47

^a (g/100 cc)⁻¹, in methyl ethyl ketone at 25°.

¹ G. Gee, *Trans. Faraday Soc.* **38**, 48 (1942); G. Gee and W. J. C. Orr, *Trans. Faraday Soc.* **42**, 507 (1946); Meyer, Wolff, and Boissonas, *Helv. Chim. Acta* **23**, 430 (1940).

² M. Schick, Ph.D. thesis, Polytechnic Institute of Brooklyn, 1948; private communication from Professor B. H. Zimm.

³ In collaboration with Mr. W. M. Sawyer.

⁴ M. L. Huggins, *J. Am. Chem. Soc.* **64**, 2716 (1942).

⁵ We are much indebted to Mr. Edward L. Foster for these measurements.

⁶ P. M. Doty and E. Mishuck, *J. Am. Chem. Soc.* **69**, 1631 (1947).

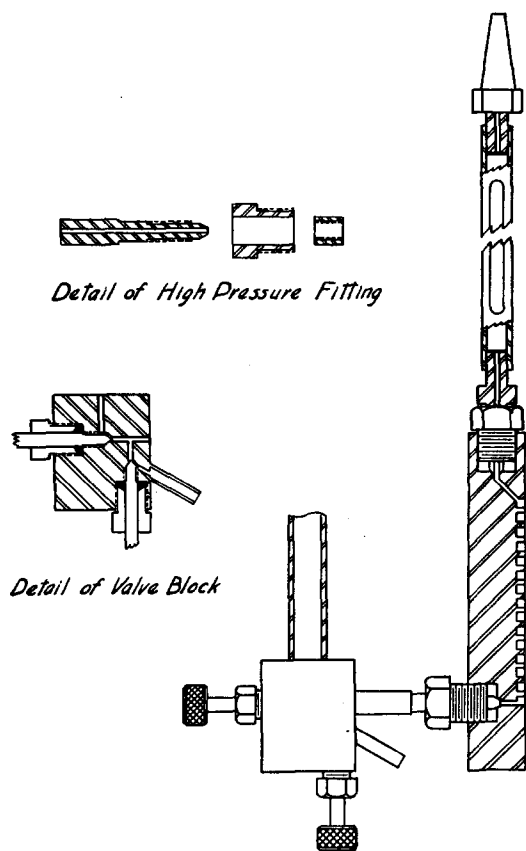


FIG. 1. Stainless steel osmometer.

volume of pure solvent; in subsequent calculations this is assumed to be the case for solutions of Fraction II as well as of the whole polymer. The partial specific volume of polymer, \bar{v}_2 , is in each case close to the value (0.840) given by the reciprocal of the density of the pure polymer as listed by the manufacturer. Its temperature dependence (expansivity of about 5×10^{-4} per degree) appears to be about twice that of polystyrene in toluene.⁷

Dioxane (Carbide and Carbon Chemicals Corporation) was purified by refluxing with hydrochloric acid, neutralization, and distillation over sodium. Methyl ethyl ketone (Carbide and Carbon Chemicals Corporation) and 1,2,3-trichloropropane (Shell Chemical Corporation⁸) were dried over sodium sulfate and distilled through a 30-plate Oldershaw column. Acetone (C. P. grade) and dimethyl phthalate (Eastman) were used without further purification.

METHOD

Apparatus

An osmometer of the Flory type⁹ was constructed of stainless steel, type 316, No. 4Mo. A few modifications

⁷ R. F. Boyer and R. S. Spencer, *J. Polymer Sci.* 3, 97 (1948).

⁸ We are indebted to the Shell Chemical Corporation for a complimentary sample of this solvent.

⁹ P. J. Flory, *J. Am. Chem. Soc.* 65, 372 (1943).

were introduced (see Fig. 1). Valves are provided both for filling and for draining the cells, to obtain samples for analysis after equilibration. The conical valve stems are hardened stainless steel (Allegheny 2EZ type 416). Each capillary (0.5 mm), instead of being affixed by a fragile metal-to-glass seal, is enclosed by a stainless steel sleeve and is forced against the osmometer block by pressure from a nut at the top of the sleeve, a lead washer being inserted at each end of the glass tube.¹⁰ Channels are cut in the sleeve to permit observation. The entire osmometer is immersed in a water thermostat regulated to 0.003°C, the capillaries and filling tubes projecting only an inch above the water level. Stainless steel straps attached to the blocks serve for handling. For measurements of osmotic pressures greater than 15 cm of solvent, the solution side of the osmometer can be connected by pressure tubing to a mercury manometer. The manometer is also connected to a 4 l. reservoir of air immersed in the thermostat, to avoid pressure changes due to slight volume changes in the tubing occasioned by fluctuations in room temperature, which would upset attainment of osmotic equilibrium.

Membranes

DuPont Cellophane No. 600 was soaked overnight in 30 percent sodium hydroxide, washed for a few minutes in progressive dilutions of sodium hydroxide and in water, and stored in 50 percent aqueous trimethylene glycol. The progressive dilutions of alkali were essential to avoid wrinkling of the membrane. After being clamped in the osmometer, the membrane was conditioned to the solvent by repeatedly filling and draining both sides of the osmometer.

A measure of the rapidity of approach to equilibrium in various solvents was afforded by noting the rates of hydrostatic adjustment with solvent on both sides of the membrane. Plots of the natural logarithm of the difference in height in the two capillaries against time gave straight lines in every case (except for acetone, where the initial slope is recorded); the slopes in hr^{-1} were as follows: acetone, 3.8; methyl ethyl ketone, 3.8; dioxane, 1.5; 1,2,3-trichloropropane, 0.7; dimethyl phthalate, 0.07; toluene, 0.005. These values reflect, primarily, different porosities of the membrane swollen to equilibrium in the different solvents. Osmotic studies in dimethyl phthalate are feasible, in spite of its high viscosity; but not in toluene with this type of membrane.

The dependence of porosity on solvent was also indicated by the ease of diffusion of low molecular weight components of the unfractionated polymer through the membrane. In acetone and methyl ethyl ketone, as much as 2 percent of the polymer was recovered on the solvent side of the membrane after equilibration, while in dioxane and 1,2,3-trichloropropane no such diffusion occurred.

¹⁰ This design was based on discussions with Dr. M. Wales, formerly of the U. S. Rubber Company.

TABLE II. Data from osmotic pressure measurements in dilute solution.

Polymer	Solvent	Temperature	$\bar{M}_n \times 10^{-3}$	μ	$A_2 \text{ cm}^3 \text{g}^{-2} \times 10^4$
Unfractionated	Acetone	25°	140	0.437	6.0
	Methyl ethyl ketone	25°	150	0.429	5.6
	Dioxane	25°	130	0.407	7.8
	Dioxane+5 percent dimethyl phthalate	25°	130	0.407	7.8
	Dimethyl phthalate	25°	—	0.400	5.0
Fraction I	Methyl ethyl ketone	25°	840	0.44	5
Fraction II	Methyl ethyl ketone	10°	300	0.43	5.3
		45°	300	0.43	5.0
		15°	270	0.38	8.0
	Trichloropropane	50°	270	0.38	8.0
Fraction III	Methyl ethyl ketone	25°	62	0.41	6.8

Equilibration of Impurities of Low Molecular Weight

To determine the effect of solvent impurities, equilibrations were made with pure dioxane against 1 percent solutions of water, dimethyl phthalate, and toluene in dioxane. Before each equilibration, the membrane was conditioned by standing overnight with the corresponding solution in both cells of the osmometer. In each case a difference in height of several centimeters was attained in about one hour, and subsequently fell to zero in about ten hours. The temporary pressure increase appeared on the solution side for the dimethyl phthalate and toluene solutions, but on the solvent side for the water solution, indicating that the water diffused more rapidly than the dioxane. These results emphasize the importance of solvent purity, and of protecting hygroscopic solvents from contact with water vapor.

It is of interest that, although toluene passes very slowly through a membrane immersed in pure toluene, toluene molecules in dilute solution diffuse readily through a membrane swollen in dioxane.

Details of Procedure

The difficulties with air bubbles described by others who have used 0.5 mm capillaries were eliminated by introducing small puffs of air with a rubber bulb at the tops of the capillaries between draining and refilling the cells. After puffing five times at five minute intervals, one fills the cells slowly by opening the filling tube valves, and then the drain valves are opened briefly to allow a few drops of liquid to escape before closing the filling valves.

Air was removed from each solution before loading by warming and briefly reducing the pressure until boiling occurred. The resulting change in concentration was of no consequence, because the final concentration was determined after equilibration. Each cell was drained, rejecting the first cc which represented the dead space between cell and valve; the liquid from the solution side was analyzed by dry weight in vacuum at 100°, and the solvent was also frequently analyzed to determine

whether any diffusion across the membrane had occurred.

With unfractionated polymer, about 2 percent of the solute was recovered on the solvent side after twelve hours in methyl ethyl ketone, but none in dioxane. With Fraction II, about 1 percent was recovered after twenty-four hours in methyl ethyl ketone; since equilibrations required only three hours, this was considered negligible. In trichloropropane, equilibrations required about twelve hours, but no diffusion into the solvent side occurred within this period.

RESULTS

The unfractionated polymer and the fractions were studied in dilute solution in several solvents.¹¹ Fraction II was studied in methyl ethyl ketone at 10°, 25°, and 45°, and in 1,2,3-trichloropropane at 15° and 50° over an extended concentration range. The column heights were converted to pressures in g/cm², using the density

TABLE III. Osmotic pressures of Fraction II in methyl ethyl ketone.

10°		25°		45°	
conc., g/cc	π g/cm ²	conc., g/cc	π g/cm ²	conc., g/cc	π g/cm ²
0.0052	0.77	0.0052	0.80	0.0076	1.50
0.0076	1.39	0.0074	1.40*	0.0078	1.59
0.0129	3.31*	0.0124	3.33	0.0081	1.75
0.0148	4.26	0.0127	3.35	0.0092	2.06
0.0194	7.02*	0.0128	3.45	0.0125	3.50
0.0315	19.0	0.0140	4.12	0.0126	3.52
0.0321	19.8	0.0146	4.28	0.0141	4.30*
0.0479	46.4	0.0165	5.36	0.0192	7.27
0.0572	66.6	0.0190	7.12*	0.0208	8.86
0.0590	73.1	0.0420	35.9	0.0274	15.3
0.0645	87.6	0.0421	35.9	0.0285	16.9
		0.0732	119.1	0.0351	26.1
				0.0453	45.7
				0.0563	73.0
				0.0675	108.0

* Average of duplicate determinations.

TABLE IV. Osmotic pressures of Fraction II in 1,2,3-trichloropropane.

15°		50°	
conc., g/cc	π g/cm ²	conc., g/cc	π g/cm ²
0.0054	1.23	0.0080	2.39
0.0074	1.96	0.0086	2.70
0.0110	4.06	0.0094	3.14
0.0112	4.12	0.0114	4.74
0.0135	5.67	0.0150	7.88
0.0171	8.95	0.0151	8.00
0.0205	13.85	0.0194	13.25
0.0217	15.00	0.0196	13.66
0.0220	15.11	0.0217	17.00
0.0224	17.10	0.0236	20.6
0.0301	32.5	0.0292	33.1
0.0327	39.4	0.0309	38.2
0.0381	55.8	0.0335	45.6
0.0413	67.1	0.0342	46.9
0.0592	156.5	0.0395	63.8

¹¹ We are much indebted to Mr. Lester D. Grandine, Jr. and Mr. W. W. Evans for help with these measurements.

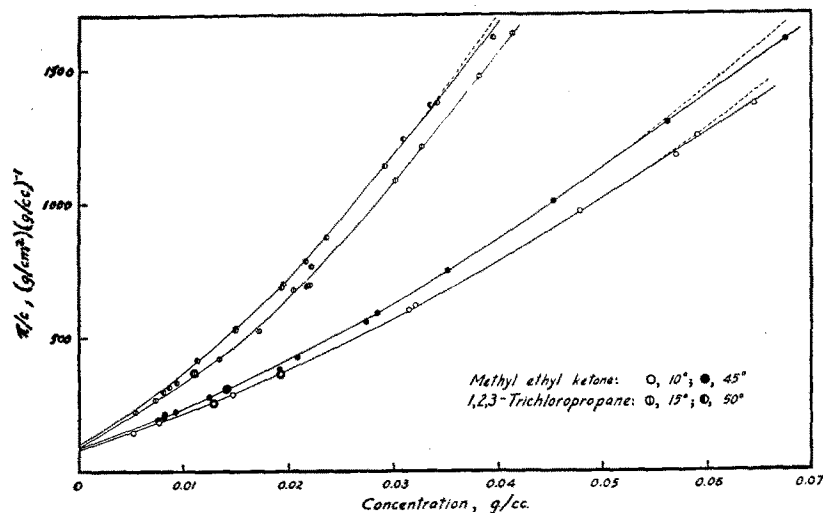


FIG. 2. Osmotic pressures of polyvinyl acetate solutions. Plots of π/c against c in 1,2,3-trichloropropane and methyl ethyl ketone. Dashed lines are calculated from Eq. (1) with the coefficients of Table VII.

TABLE V. Thermodynamic data for Fraction II in methyl ethyl ketone.

w_2	$\Delta\bar{H}_1$ cal./mole, $\times 10^3$	$\Delta\bar{S}_1$ cal./deg. mole, $\times 10^5$	25°C				\bar{v}_2	$\frac{\Delta\bar{H}_1}{\bar{v}_2^2}$	$\frac{\Delta\bar{S}_1}{\bar{v}_2}$
			$-\Delta\bar{F}_1:$ $-\Delta\bar{H}_1$ $\pi\bar{V}_1$ $\times 10^3$	$-\Delta\bar{F}_1:$ $-(\Delta\bar{H}_1 - T\Delta\bar{S}_1)$ $\times 10^3$	\bar{v}_2	\bar{v}_2			
0.005	-0.024	0.29	0.13	0.11	0.0034	-22	0.0009		
0.010	-0.11	0.74	0.33	0.33	0.0068	-24	0.0011		
0.0175	-0.29	1.88	0.87	0.85	0.0118	-23	0.0016		
0.025	-0.72	3.57	1.67	1.78	0.0170	-25	0.0021		
0.035	-1.8	5.1	3.34	3.3	0.0238	-33	0.0021		
0.045	-2.3	11.7	5.75	5.8	0.0307	-25	0.0038		
0.055	-3.0	19.5	8.95	8.8	0.0377	-21	0.0051		
0.065	-6.1	22.2	12.9	12.7	0.0447	-30	0.0050		
0.075	-7.1	33.0	17.5	16.9	0.0517	-28	0.0064		
					avg.	-26			

TABLE VI. Thermodynamic data for Fraction II in 1,2,3-trichloropropane.

w_2	$\Delta\bar{H}_1$ cal./mole, $\times 10^3$	$\Delta\bar{S}_1$ cal./deg. mole, $\times 10^5$	30°C				\bar{v}_2	$\frac{\Delta\bar{H}_1}{\bar{v}_2^2}$	$\frac{\Delta\bar{S}_1}{\bar{v}_2}$
			$-\Delta\bar{F}_1:$ $-\Delta\bar{H}_1$ $\pi\bar{V}_1$ $\times 10^3$	$-\Delta\bar{F}_1:$ $-(\Delta\bar{H}_1 - T\Delta\bar{S}_1)$ $\times 10^3$	\bar{v}_2	\bar{v}_2			
0.005	-0.23	0.73	0.47	0.45	0.0058	-68	0.0012		
0.0075	-0.31	2.08	0.93	0.93	0.0087	-42	0.0024		
0.010	-0.51	3.7	1.6	1.6	0.0115	-38	0.0032		
0.015	-1.57	7.0	3.6	3.6	0.0173	-52	0.0040		
0.020	-3.8	10.6	7.0	7.0	0.0231	-70	0.0046		
0.025	-7.3	13.9	11.5	11.4	0.0288	-82	0.0059		
0.029	-10.0	20.2	16.0	16.0	0.0335	-89	0.0062		

TABLE VII. Coefficients for power series in c .

Solvent	Temperature	A_2 cm^3g^{-2}	A_3 cm^6g^{-3}
Methyl ethyl ketone	10°	5.3×10^{-4}	5.2×10^{-3}
	45°	5.0×10^{-4}	5.4×10^{-3}
1,2,3-trichloropropane	15°	8.0×10^{-4}	17.6×10^{-3}
	50°	8.0×10^{-4}	16.4×10^{-3}

data given above for methyl ethyl ketone and trichloropropane, and, for the other solvents, values calculated on the assumption of additivities of the volumes of polymer and solvent.

Measurements in Dilute Solution

The results for dilute solutions in acetone, methyl ethyl ketone, 1,2,3-trichloropropane, dioxane, dimethyl phthalate, and a 5 percent solution of dimethyl phthalate in dioxane, are summarized in Table II. Plots of π/c against c gave straight lines for the unfractionated polymer and Fraction III; for Fraction II (Fig. 2) and Fraction I there was upward curvature, in the latter case sufficient to make extrapolation somewhat uncertain. The molecular weights were calculated from the intercepts; the slopes are described both by the value of μ as used by Huggins,¹² and by the coefficient A_2 of Zimm.¹³ No particular significance is attached to the fact that the values of M_n for different solvents do not appear to be quite identical, the differences being probably within experimental error.

It is clear that trichloropropane is much the best solvent, while the others are all roughly comparable. Our value of μ in acetone agrees well with that obtained by Sirianni, Wise, and McIntosh¹⁴ (0.439), while our value in trichloropropane agrees with theirs in chloroform (0.377), suggesting an interaction characteristic of chlorinated hydrocarbons. A slight decrease in A_2 with increasing molecular weight is observed in methyl ethyl ketone, as predicted by the theories of Zimm¹³ and Flory¹⁵ for dilute solutions.

Measurements in Moderately Concentrated Solution

The results for more concentrated solutions of Fraction II in methyl ethyl ketone and trichloropropane are

¹² M. L. Huggins, J. Am. Chem. Soc. **64**, 1712 (1942).

¹³ B. H. Zimm, J. Chem. Physics **14**, 164 (1946).

¹⁴ Sirianni, Wise, and McIntosh, Can. J. Research **25B**, 301 (1947).

¹⁵ P. J. Flory, J. Chem. Phys. **13**, 453 (1945).

given in Tables III and IV. The ratio π/c is plotted against c in Fig. 2; even at these moderate concentrations, it attains values enormously greater than the extrapolated, or ideal, value of π/c . It rises far more steeply in trichloropropane than in methyl ethyl ketone.

DISCUSSION

Coefficients for Power Series in c

In a treatment of the statistical mechanics of large molecules, Zimm¹³ has expressed the osmotic pressure by the power series

$$\pi = RT(c/M_2 + A_2c^2 + A_3c^3 + \dots). \quad (1)$$

The curves of Fig. 2 can be fitted by Eq. (1), using three terms; the coefficients are tabulated in Table VII. In Fig. 2, the calculated curves are indistinguishable from the experimental curves except for a slight divergence at the highest concentrations, where they are shown by

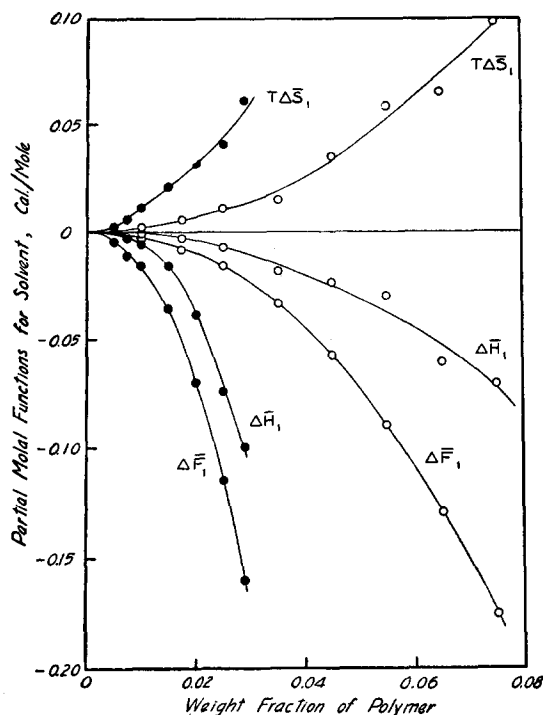


FIG. 3. Derived thermodynamic functions plotted against weight fraction of polymer. O, methyl ethyl ketone; ●, 1,2,3-trichloropropane.

broken lines. In trichloropropane, A_2 is larger and A_3 is much larger than in methyl ethyl ketone.

Derived Thermodynamic Data

The partial molal heat, entropy, and free energy of dilution of the solvent may be calculated by the equations¹

$$\Delta \bar{H}_1 = \frac{T'(\pi \bar{V}_1)_T - T(\pi \bar{V}_1)_{T'}}{T - T'}, \quad (2)$$

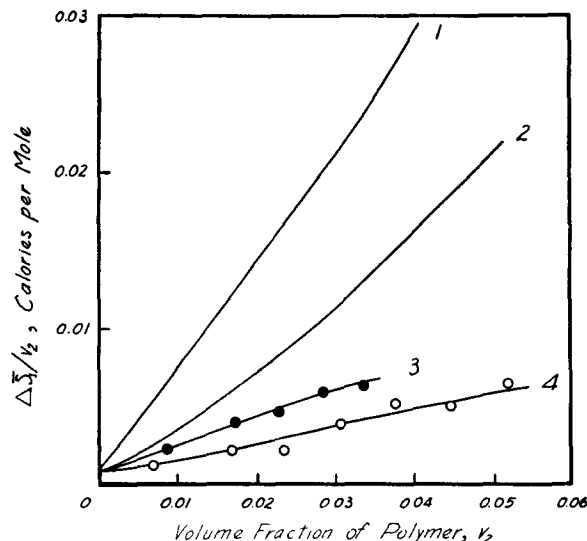


FIG. 4. Plots of $\Delta \bar{S}_1/v_2$ against v_2 . 1, lattice theory; 2, rubber in benzene (Gee and Treloar); 3, polyvinyl acetate in 1,2,3-trichloropropane; 4, polyvinyl acetate in methyl ethyl ketone.

$$\Delta \bar{S}_1 = \frac{(\pi \bar{V}_1)_T - (\pi \bar{V}_1)_{T'}}{T - T'}, \quad (3)$$

$$\Delta \bar{F}_1 = -\pi \bar{V}_1, \quad (4)$$

where T and T' refer to two absolute temperatures, and the osmotic pressures are taken at constant weight fraction (w_2). These quantities have been derived from values of π interpolated from the experimental curves in Fig. 2 at concentrations corresponding to selected values of the weight fraction, and they are tabulated in Tables V and VI. The values of $\Delta \bar{F}_1$ refer to an intermediate temperature in each case; the agreement between $-\pi \bar{V}_1$ and $\Delta \bar{H}_1 - T\Delta \bar{S}_1$ indicates the precision of the differencing operations, which is quite satisfactory. Values of $\Delta \bar{H}_1/v_2^2$ and $\Delta \bar{S}_1/v_2$, where v_2 is the volume fraction of polymer, are also included. In Fig. 3, the thermodynamic functions are plotted against w_2 .

Heat of Dilution

The heats of dilution are all negative. In the case of methyl ethyl ketone $\Delta \bar{H}_1$ is proportional to v_2^2 over the range studied. This relationship cannot be explained by the usual treatment of cohesive energy densities, of course, which holds only for positive heats of mixing. In trichloropropane $\Delta \bar{H}_1/v_2^2$ is at least twice as great as in the ketone, and increases somewhat with increasing concentration. This greater interaction with the chlorinated compound recalls the negative deviations from ideality in the system acetone-chloroform,¹⁶ and the negative heat of dilution of cellulose acetate-tetrachloroethane.¹⁷

¹⁶ S. Glasstone, Trans. Faraday Soc. **33**, 200 (1936).

¹⁷ O. Hagger and A. J. A. van der Wyck, Helv. Chim. Acta **23**, 484 (1940).

Entropy of Dilution

In Fig. 4, our values of $\Delta\bar{S}_1/v_2$ are plotted against v_2 , together with the data of Gee for rubber in benzene and the theoretical curve given by the lattice theory.¹⁸ The experimental values are all considerably smaller than the theoretical, as Flory¹⁵ points out is generally the case in dilute solutions. The entropies of dilution in the case of polyvinyl acetate are even smaller than those for rubber.

It is of interest to compare the initial slopes in Fig. 4 with those calculated from the theory of Flory in which the entropy of dilution is related to the volume of a coiled molecule as estimated from intrinsic viscosity.¹⁵ The intrinsic viscosities⁹ of Fraction II are 0.98 in methyl ethyl ketone and 1.35 in trichloropropane; the corresponding initial slopes from the theory are 29 and 43 cal./deg.-mole, respectively, while the observed values are 26 and 52. The agreement indicates that the higher entropy of dilution in trichloropropane may be due primarily to a more extended configuration of the polymer molecule, at least in very dilute solution.

¹⁸ Reference 15, Eq. (4'') (assuming $z=6$).

In more concentrated solution, it might have been anticipated that the larger negative heat of dilution in trichloropropane would be accompanied by an ordering of the solvent by interaction with the polymer so that the entropy of dilution would be smaller than in methyl ethyl ketone. Nevertheless, $\Delta\bar{S}_1$ is higher in trichloropropane over the whole concentration range studied.

A more detailed interpretation may be facilitated by accumulation of similar thermodynamic data for concentrated solutions of other polymer systems. Correlations with mechanical properties will be given subsequently.

ACKNOWLEDGMENT

This work was supported in part by the Research Committee of the Graduate School of the University of Wisconsin from funds supplied by the Wisconsin Alumni Research Foundation, and in part by a grant from Research Corporation. We wish to thank Professor J. W. Williams for the use of a high precision cathetometer. We are especially indebted to Professor Bruno H. Zimm, University of California, for helpful suggestions in interpretation of the data.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 17, NUMBER 11 NOVEMBER, 1949

A Theory of Vapor Pressures of Liquids Based on van der Waals' Equation of State. II. Binary Mixtures¹

FREDERICK T. WALL AND GUNTHER S. STENT*

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

(Received April 4, 1949)

An expression for vapor pressures of binary liquid systems obeying van der Waals' equation of state is developed by generalizing a recent theory of vapor pressures of pure liquids. The resulting partial vapor pressure equations involve composition and temperature, and contain no empirical quantities other than van der Waals' constants including an inter-species interaction term.

The conditions under which Raoult's law holds for these systems are formulated, together with the conditions for which positive or negative deviations occur. The compositions at which azeotropes form are predicted, and the partial miscibility of binary liquid systems is discussed. A number of examples are calculated to illustrate the theory.

INTRODUCTION

IN a previous paper¹ an expression was derived for the vapor pressure of a liquid, assuming the validity of van der Waals' equation of state and involving the use of an appropriate mathematical expression for the volume of a van der Waals' liquid. It was also shown that certain empirical laws, such as those of Trouton and Guldberg-Guye, could be deduced qualitatively. It is the purpose of the present paper to extend the vapor pressure treatment to binary mixtures of liquids and to compare the resulting vapor pressure equations with certain well-known rules, such as Raoult's and Henry's laws.

A theory of vapor pressures of binary mixtures obeying van der Waals' equation of state has already been developed by van Laar,² who employed methods similar to those of the present treatment but did not make use of a theory of vapor pressures of pure liquids. It is in this connection that the present development offers certain advantages, for vapor pressure relationships are derived involving no empirical quantities other than van der Waals' constants. Recently Wang³ also discussed the behavior of van der Waals' fluids with some reference to mixtures.

Let us consider a mixture of two fluids and assume that a continuous transition from the gaseous to the

* Present address: Kerckhoff Laboratories of Biology, California Institute of Technology, Pasadena 4, California.

¹ F. T. Wall, *J. Chem. Phys.* **16**, 508 (1948).

² J. J. van Laar, *Zeits. f. physik. Chemie* **72**, 723 (1910); **83**, 599 (1913).

³ J. S. Wang, *Chinese J. Phys.* **6**, 27 (1945).