[CONTRIBUTION FROM GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

A Study of the Interaction of Nitrocellulose with Some Solvents and Non-solvents by the Light-Scattering Method[1]

BY ROBERT H. BLAKER AND RICHARD M. BADGER

A recent paper by Ewart, Roe, Debye and McCartney[2] on the light scattering of polymers dissolved in binary mixtures suggested to us that light scattering studies should yield interesting information regarding the interaction of polymer not only with good solvents but with plasticizers which are solid or have high viscosity and indeed with non-solvents, provided both polymer and the other substance can be dissolved in a common solvent. As was shown by the above mentioned authors the addition of a third component to a polymer solvent mixture should in general cause a change in light scattering even in the absence of association, due to preferential adsorption of one or other of the solvent components by the polymer. If the solvent component adsorbed has the higher refractive index the ratio of polymer concentration to turbidity, in the limit of zero concentration, should decrease. The opposite will be true if the refractive indices are in the reverse order.

Since we have been for some time concerned with the interactions of nitrocellulose with various substances, studies were consequently undertaken to determine the capacity of the light scattering method for their quantitative investigation. The results obtained are quite different from those reported by ERDM,[2] and since at first sight they seem rather anomalous we believe they may be of general interest.

Since the experimental work here described was begun, three further treatments of the light scattering of multicomponent systems have been made independently,[3,4,5] which permit one to express the results of light scattering measurements in the language of thermodynamics, and to obtain expressions representing the dependence of the activity of the polymer on the concentrations of the respective solvent components. Since we were first acquainted with the work of Kirkwood and Goldberg we shall use their notation in the subsequent discussion.

As predicted by these authors and verified by our experiments, in a solution of nitrocellulose in a mixture of "primary" solvent and an "additive," the dependence of the turbidity τ on the respective concentrations is, up to moderate concentrations, adequately represented by an equation of the form

$$(H_2C_2/\Delta\tau) = (1/M_2)(1 + G_{10}C_1 + G_{01}C_2 + G_{20}C_1^2 + G_{11}C_1C_2 + G_{02}C_2^2) \quad (1)$$

where $\Delta\tau$ is the difference in turbidities of the total solution and of the binary solvent, C_2 is the concentration of polymer in the solution and C_1 of the "additive" in both the solution and the binary solvent, each expressed in g. per g. of primary solvent. M_2 is the molecular weight of the polymer. The expression for H_2

$$H_2 = \frac{32\pi^3 n^2}{3N\rho_0\lambda^4}\left(\frac{\partial n}{\partial C_2}\right)^2$$

is similar to that occurring in the light scattering equation for binary systems, except that the refractive index increment, $(\partial n/\partial C_2)$, is measured in the binary solvent under discussion and ρ_0 is defined as the mass of primary solvent per unit volume of solution.

Now if the activity coefficient[6] of either the polymer solute, γ_2, or of the solvent additive, γ_1, is represented by an expansion of the form

$$\ln \gamma_i = A_{ii}C_i + A_{ij}\,C_j + B_{iii}C_i^2 + B_{iij}C_iC_j +, \text{etc.} \quad (2)$$

it has been shown by Kirkwood and Goldberg that the coefficients of this expansion are related to those of Equation 1. Specifically

$$\left.\begin{aligned} &A_{21} = G_{10}M_2/2\alpha_0M_1;\ A_{22} = G_{01};\ B_{222} = G_{02}/2 \\ &B_{211} = (M_2/4\alpha_0M_1)\{G_{20} + G_{10}[A_{11} - (\alpha_1/\alpha_0) - (3G_{10}/4)]\} \\ &B_{212} = [M_2/(2M_2 + 4M_1\alpha_0)][G_{11} + (M_2G_{10}^2/4M_1\alpha_0^2) - G_{10}G_{01} - (\alpha_2G_{10}/\alpha_0)] \\ &(A_{12}/A_{21}) = (B_{112}/B_{211}) = (B_{122}/B_{221}) = (M_1/M_2) \end{aligned}\right\} \quad (3)$$

In the above, M_1 is the molecular weight of the solvent additive, and the α's are coefficients in the expansion relating the ratio of refractive index increments to concentration

$$\left(\frac{\partial n}{\partial C_1}\right)\bigg/\left(\frac{\partial n}{\partial C_2}\right) = \alpha_0 + \alpha_1C_1 + \alpha_2C_2 \quad (4)$$

Though the coefficient A_{11} can in principle be determined from light scattering measurements we found it more convenient to obtain it from vapor pressure measurements by one of the relations

$$A_{11} = \lim_{C_1\to 0}\frac{\mathrm{d}\ln(p_1/C_1)}{\mathrm{d}C_1} = -(M_1/M_0)\lim_{C_1\to 0}\frac{\mathrm{d}^2\ln p_0}{\mathrm{d}C_1{}^2} \quad (5)$$

where p_1 and p_0 are the partial vapor pressures of solvent additive and major component, respec-

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[1] Contribution No. 1363 from the Gates and Crellin Laboratories of Chemistry. The work here described was supported by the Bureau of Ordnance through the Office of Naval Research under Contract N6-ori-102, VI.

[2] R. H. Ewart, C. P. Roe, P. Debye and J. R. McCartney, *J. Chem. Phys.*, **14**, 687 (1946).

[3] H. C. Brinkman and J. J. Hermans, *J. Chem. Phys.*, **17**, 574 (1949).

[4] J. G. Kirkwood and R. J. Goldberg, *ibid.*, **18**, 54 (1950).

[5] W. H. Stockmayer, *ibid.* **18**, 58 (1950).

[6] The activity coefficient is defined by the relation of the thermodynamic potential to concentration: $\mu_i = RT \ln \gamma_iC_i + \mu_i^*(T, p)$ where μ_i^* is so chosen that γ_i approaches unity as C_i approaches zero.

tively above their mixtures. The second relation was used when the additive had low volatility.

Materials and Experimental Procedures

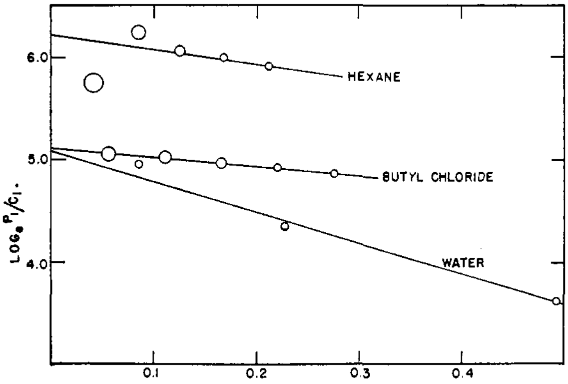
The nitrocellulose used was a commercial gun cotton which has been used in numerous investigations in this Laboratory (Hercules No. 8432, 12.67% nitrogen, $[\eta] = 2.65$ (in acetone), $\overline{M}_{wt} = 75{,}000$). Though the nitrocellulose used was polydisperse and the various coefficients evaluated below are consequently to be regarded as average values, it is not believed that they differ greatly from those for a monodisperse fraction of the same average molecular weight. We have never found that polydispersity is in any way reflected in light scattering measurements, and indeed the coefficient G_{01} of Eqn. 1 is rather insensitive to molecular weight.

The major solvent constituent was in each case acetone; the solvent additives were water, ligroin (b. p. 60–70°), *n*-butyl acetate, *s*-butyl chloride, and diethyl phthalate, which were chosen for reasons discussed below. With the exception of the ligroin all solvents were C. P. grade.

Light scattering measurements were made at approximately 25° with the 90° photometer and with the techniques described in a previous article.[7] The turbidities were calculated from the 90° scattering alone, since the asymmetry of scattering, although appreciable ($q = 1.22$), was not sensibly changed by the addition of the second solvent component.

Owing to the different rates of evaporation of the two solvent components extreme care had to be exercised both in making the rather elaborate series of refractive index measurements required, and in centrifugation of the solutions for turbidity measurements. In the latter case errors were reduced by centrifugation in a sealed rotor in a refrigerated centrifuge.

In order to determine the constants A_{11}, measurements of partial vapor pressures were made on each binary solvent except water–acetone, for which data are given in the literature.[8,9] A modification of the dynamic method of Washburn[10] was used. The data for the volatile additives are given in Fig. 1. In these vapor pressure measurements *n*-hexane was actually employed rather than ligroin, but the coefficient A_{11} is presumably not greatly different for the two substances. The points for the non-volatile additives, diethyl phthalate and butyl acetate, showed considerable scatter and warrant only the conclusion that A_{11} is small.

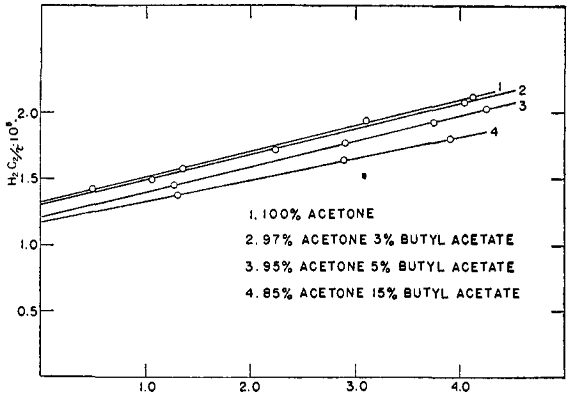


C_1, grams per gram of acetone.

Fig. 1.

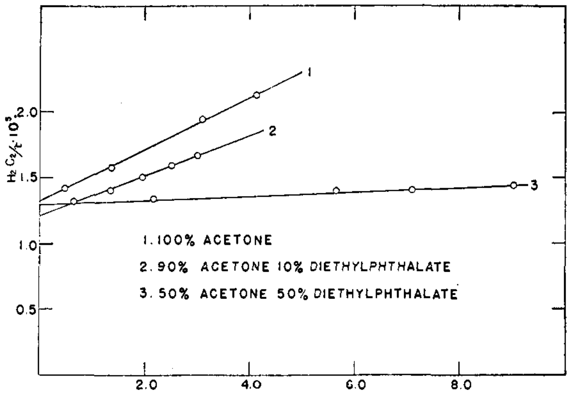
Experimental Results

The results of the light scattering experiments are shown in Figs. 2–6 which present plots of H_2C_2/τ *versus* C_2, the nitrocellulose concentration, for several values of C_1, the concentration of the solvent additive. In the first two figures the additive was either a solvent or plasticizer for nitrocellulose (butyl acetate and diethyl



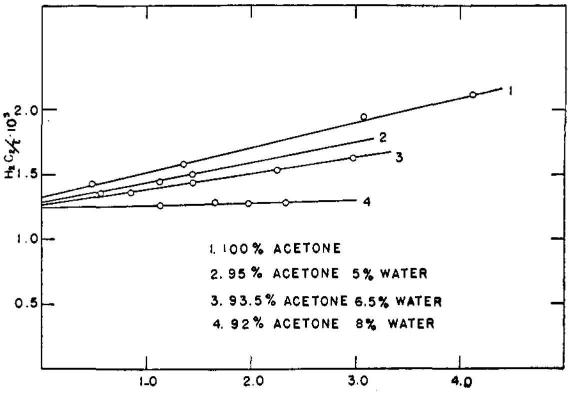
$C_2 \times 10^3$.

Fig. 2.



$C_2 \times 10^3$.

Fig. 3.



$C_2 \times 10^3$.

Fig. 4.

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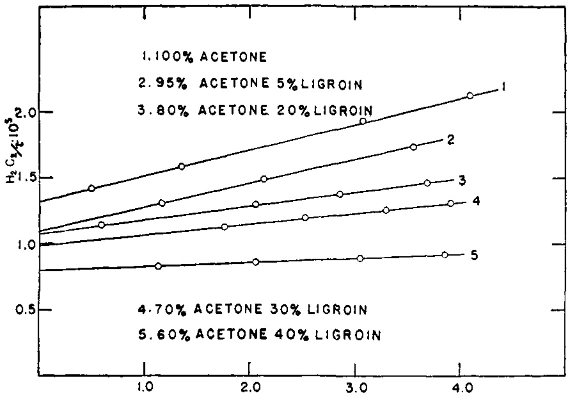
[7] R. H. Blaker, R. M. Badger and T. S. Gilman, *J. Phys. and Coll. Chem.*, **53**, 794 (1949).

[8] W. G. Beare, G. A. McVicar and J. B. Ferguson, *J. Phys. Chem.*, **34**, 1310 (1930).

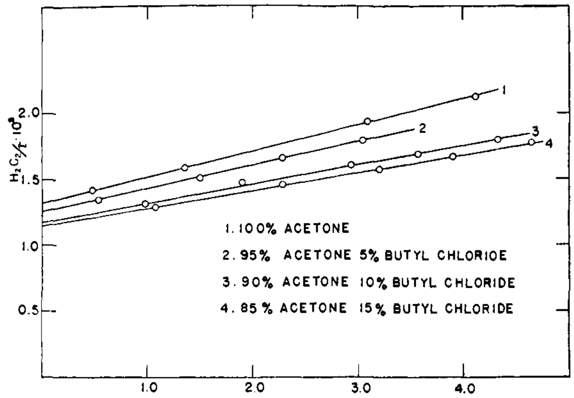
[9] G. L. Wilson and F. D. Miles, *Trans. Roy. Soc. (London)*, **A233**, 247 (1934).

[10] E. W. Washburn and E. O. Heuse, THIS JOURNAL, **37**, 309 (1915).



$C_2 \times 10^3$.

Fig. 5.



$C_2 \times 10^3$.

Fig. 6.

phthalate). In the other cases it was a non-solvent or precipitant. All solvent additives had greater refractive indices than acetone except water, for which the index is nearly identical. A comparison of the curves for butyl acetate and butyl chloride is of interest since these substances have nearly equal refractive indices but differ greatly in solvent properties for nitrocellulose.

In Table I are given the coefficients of Eqns. 1 and 4 for each system, and also those of Eqn. 2, expressing the activity coefficient of nitrocellulose as a function of concentration.

TABLE I

THERMODYNAMIC AND REFRACTIVE INDEX CONSTANTS FOR NITROCELLULOSE SOLUTIONS

Solvent additive	*s*-Butyl acetate	Diethyl phthalate	Water	Ligroin	*n*-Butyl chloride
Constant			Light Scattering Equation		
G_{10}	−1.7	−0.6	−0.5	−1.7	−0.8
G_{01}	150	150	150	150	150
G_{11}	−50	−330	−350	−340	−360
G_{20}	5.3	0.4	0	2.0	0
G_{02}	0	0	0	0	0
			Refractive Index Equation		
α_0	0.26	1.03	0.82	0.15	0.26
α_1	0.30	0.58	−2.8	0.14	0.30
α_2	0	0	0	0	0
			Expression for Activity Coefficient		
$A_{21} \times 10^{-3}$	−2.0	−0.1	−1.4	−5.0	−1.1
$A_{22} \times 10^{-2}$	1.5	1.5	1.5	1.5	1.5
$B_{211} \times 10^{-3}$	(3.1)	(0.04)	−0.6	5	0.7
$B_{212} \times 10^{-4}$	0.3	−0.01	0.01	1.4	0.07
B_{222}	0	0	0	0	0
A_{11}	∼0	∼0	−3	−1 (hexane)	−0.6

It will be noted that in each case the intercept of the light scattering curve was reduced by the solvent additive, independent of whether this material was a solvent or non-solvent. The coefficient A_{21} is negative for each solvent additive.

Discussion

Though the curves shown in Figs. 2–6 are similar in appearance to those presented by ERDM,[2] they have quite the opposite significance since in all our systems the refractive index of the solvent additive is greater than that of the primary solvent. Evidently at low concentrations the activity of the nitrocellulose was reduced by each of the additives, whether solvent or non-solvent in the ordinary sense.

In terms of the ERDM theory the additive is in each case positively adsorbed by the polymer. In the case of the non-solvents the magnitude of the effect may at first seem surprising though its sign could probably have been anticipated from previous observations in the literature. Measurements on rates[11] and heats[12] of solution have indicated rather strong interaction between nitrocellulose and non-solvents, as have also vapor pressure measurements on acetone–water solutions.[9]

The fact that both polar and non-polar substances may interact strongly with nitrocellulose is presumably due to the character of the nitrocellulose molecule which may roughly be visualized as a ribbon with polar groups along the edges, but with non-polar faces.

It is evident that the light-scattering method offers a very powerful means for the quantitative investigation of the interaction of polymer with a great variety of substances which may be of interest in connection with problems of plasticization or in the development of systems for polymer fractionation, etc. The application of the method may be limited in some cases by difficulties presented by the light-scattering techniques and the study of some interesting systems may unfortunately not be practical because of unfavorable refractive index relations.

Summary

The thermodynamic interaction between nitrocellulose and several substances, both solvents and non-solvents, has been investigated by light-scattering observations on acetone solutions of polymer to which the substance in question was added. The additives (*n*-butyl acetate, diethyl

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[11] A. Kraus, *Farben-Chem.*, **10**, 236 (1939).

[12] T. Nakashima and N. Saito, *J. Soc. Chem. Ind. Japan*, **38**, B232 (1935).

phthalate, water, ligroin, *s*-butyl chloride) were all found to be selectively adsorbed on nitrocellulose. An expression is given for the activity of nitrocellulose as a function of its concentration and of the solvent additive.

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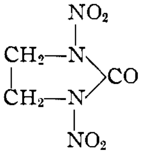
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

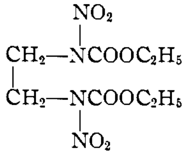
The Nitration of Derivatives of Ethylenediamine[1]

BY W. E. BACHMANN, W. J. HORTON,[2a] E. L. JENNER,[2b] N. W. MACNAUGHTON[2c] AND C. E. MAXWELL, III[2d]

Various methods were investigated for preparing the high explosive ethylenedinitramine (hereinafter called EDNA), $NO_2NHCH_2CH_2NHNO_2$, from ethylenediamine. EDNA has been prepared previously by hydrolysis of 1,3-dinitro-2-imidazolidone (I), which can be made by nitration of 2-imidazolidone. Fischer and Koch[3] prepared 2-imidazolidone by heating a mixture of anhydrous ethylenediamine and diethyl carbonate in a sealed tube; the yield was low and the product was difficult to purify. Moreover, the preparation of anhydrous ethylenediamine is a tedious process. We found that 2-imidazolidone could be obtained in 63% yield (based on the diethyl carbonate) from commercial aqueous 60–65% ethylenediamine without the use of a sealed-tube reaction. A mixture of excess aqueous ethylenediamine and diethyl carbonate was heated, the excess of reagents and water was removed by distillation, and the residue, presumably the ethylenemonourethan, $H_2NCH_2CH_2NHCOOC_2H_5$, was cyclized by the action of heat.[4]

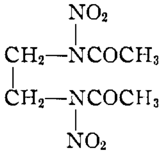
By the method of Franchimont and Klobbie[5] and of Backer[6] with modifications, EDNA was prepared from aqueous ethylenediamine in an over-all yield of 87%. In this method ethylenebisurethan, prepared from aqueous ethylenediamine and ethyl chlorocarbonate, was nitrated with 98% nitric acid, and the dinitroethylenebisurethan (II) was converted into EDNA by alkaline hydrolysis or by ammonolysis. The rapid rate of the reaction of II with aqueous ammonia at room temperature is noteworthy; in a few minutes the carbethoxy groups are removed and the water-soluble ammonium salt of EDNA is formed.


I



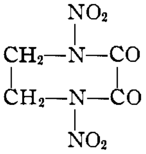
$$\begin{array}{l} \quad\;\; NO_2 \\ CH_2-NCOOC_2H_5 \\ CH_2-NCOOC_2H_5 \\ \quad\;\; NO_2 \end{array}$$

II



$$\begin{array}{l} \quad\;\; NO_2 \\ CH_2-NCOCH_3 \\ CH_2-NCOCH_3 \\ \quad\;\; NO_2 \end{array}$$

III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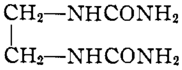
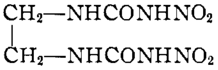


$$\begin{array}{l} CH_2-NHCONH_2 \\ CH_2-NHCONH_2 \end{array}$$

V



$$\begin{array}{l} CH_2-NHCONHNO_2 \\ CH_2-NHCONHNO_2 \end{array}$$

VI

EDNA was obtained also in good yield from the diacetyl derivative of ethylenediamine, which was prepared readily from aqueous ethylenediamine and acetic anhydride. Unlike the previous two derivatives of ethylenediamine, ethylenebisacetamide did not yield the dinitro derivative when treated with 98% nitric acid alone or mixed with concentrated sulfuric acid. A mixture of 98% nitric acid and acetic anhydride nitrated the compound smoothly. The dinitro derivative (III) was converted rapidly into EDNA by aqueous ammonia.

The powerful aid to nitration offered by acetic anhydride was again manifested in the nitration of cyclic ethyleneoxamide. van Alphen,[7] who was the first to succeed in preparing cyclic ethyleneoxamide from ethylenediamine and diethyl oxalate, found that the compound was unaffected by absolute nitric acid at 0°; by nitration at 100° he obtained a microcrystalline powder in unspecified yield which melted indefinitely at about 150° with decomposition. We obtained the dinitro derivative (IV) in good yield in the form of glistening prisms with m. p. 197–198° by nitration of cyclic ethyleneoxamide (contaminated with linear polymers) by means of 98% nitric acid and acetic anhydride at 0–5°. Ammonolysis of the dinitro compound proceeded rapidly with the formation of EDNA and oxamide.

The possibility of utilizing ethylenebisurea (V) for preparing EDNA was investigated. The only practical methods which had been described for preparing V were the reaction of ethylenediamine dihydrochloride and potassium cyanate[8] and the interaction of ethylenediamine and nitrourea.[9] We found that ethylenebisurea was

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[1] This investigation was carried out under a contract recommended by the NDRC between the OSRD and the Regents of the University of Michigan, 1940.

[2] Present addresses: (a) Department of Chemistry, University of Utah; (b) Experiment Station, du Pont de Nemours and Co.; (c) Tennessee Eastman Corp.; (d) Chas. Pfizer and Co., Inc.

[3] Fischer and Koch, *Ann.*, **232**, 227 (1885).

[4] For later preparations of 2-imidazolidone see Mulvaney and Evans, *Ind. Eng. Chem.*, **40**, 393 (1948).

[5] Franchimont and Klobbie, *Rec. trav. chim.*, **7**, 258 (1888).

[6] Backer, *ibid.*, **31**, 171 (1912).

[7] van Alphen, *Rec. trav. chim.*, **54**, 937 (1935).

[8] Dox, THIS JOURNAL, **55**, 1230 (1933).

[9] Davis and Blanchard, *ibid.*, **51**, 1790 (1929).