Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Gas Chromatographic Behavior of Aliphatic Dinitriles on Different Types of Stationary Liquid Phases

Albertine E. Habboush[a]; Nasrin M. Said[a]
[a] COLLEGE OF SCIENCE, UNIVERSITY OF BAGHDAD, BAGHDAD, IRAQ

To cite this Article Habboush, Albertine E. and Said, Nasrin M.(1979) 'Gas Chromatographic Behavior of Aliphatic Dinitriles on Different Types of Stationary Liquid Phases', Separation Science and Technology, 14: 4, 345 — 354

To link to this Article: DOI: 10.1080/01496397908057152

URL: http://dx.doi.org/10.1080/01496397908057152

SEPARATION SCIENCE AND TECHNOLOGY, 14(4), pp. 345–354, 1979

Gas Chromatographic Behavior of Aliphatic Dinitriles on Different Types of Stationary Liquid Phases

ALBERTINE E. HABBOUSH and NASRIN M. SAID

COLLEGE OF SCIENCE
UNIVERSITY OF BAGHDAD
BAGHDAD, IRAQ

Abstract

Aliphatic dinitriles were studied on different stationary liquid phases including OV-1, OV-3, OV-25, DEGS, DEGGLU, DEGA, EGTCP, Carbowax 6000, Carbowax 600, and PPG(LB-550-x). The specific retention volumes were calculated and the values were further processed in the form of heat of solutions, ΔH. These values of ΔH indicated the effect of solute–solvent interactions on the gas chromatographic behavior of these compounds and correlated with their molecular structures. Furthermore, the relationship between the viscosity of these compounds and their specific retention volumes was also considered and a general equation was derived.

INTRODUCTION

Gas chromatography has been used for the identification and separation of aliphatic mononitriles (*1*, *2*). Hor Lysyj (*3*) and Taramasse and Guerra (*4*) utilized two types of columns, polar and nonpolar, for the separation of nitriles. Mugnaini and Gambelli (*5*) separated aliphatic dinitriles on a column of Na caproate and Apiezon L on Celite, and they found the log retention time at 210°C to be directly proportional to the number of carbon atoms of the homologous series.

In this paper we present the results of a systematic investigation of aliphatic dinitriles on 11 columns of different types of stationary liquid phases. These are polyesters [polydiethylene glycol adipate (DEGA), polydiethylene glycol glutrate (DEGGLU), polydiethylene glycol succinate (DEGS), ethylene glycol tetrachlorophthalate (EGTCP)], polysiloxanes [dimethyl polysiloxane (OV-1), 10% phenyl methyl polysiloxane (OV-3), 35% phenyl methyl polysiloxane (OV-11), 75% phenyl methyl polysiloxane (OV-25)], polypropylene glycol (PPG), carbowax 600, and carbowax 6000. The forces responsible for altering the order of elution and the degree of separation are described through the values of the heats of solution and the viscosities of the solutes.

EXPERIMENTAL

Apparatus

A Beckman GC-45 gas chromatograph equipped with flame ionization detector was used. An optimal carrier gas (nitrogen) flow rate of 30 ml/min at NTP and an attenuation of 8 gave the best experimental peak shapes and heights. A Beckman model 10-mV recorder was used. The columns were made of stainless-steel tubing (6 ft long and 1/4 in. o.d.) filled with 20% w/w of the various stationary liquid phases on chromosorb W, 80–100 mesh. The column temperature was controlled to within ±0.08°.

Materials

The pure aliphatic dinitriles used in this study were obtained from BDH. No further purification was needed as each of the compounds gave only one peak with a stable base line.

Sampling

Sample sizes for the mixture ranged from 0.7 to 0.8 μl, while it was 0.1 μl for the individual liquid compounds and 0.2 μl, 50% w/w acetonic solution, for the individual solid compounds.

Results

All of the retention data measured for the dinitriles at five different column temperatures (between 130 and 170 °C) were expressed in the form of specific retention volumes (*6*), V_g^0. No difference was found in the retention times when the compounds were injected individually or in a mixture, and the results were reproducible to within ±1%. These values of specific retention volumes were further processed by linear regression so as to obtain the constants a and b of the equation

$$\log V_g^0 = (a/T) - b$$

where T is the absolute temperature of the system. The results are given in Table 1. The constant a is related to the heat of solution, ΔH, by the equation (*7–9*)

$$a = d \log V_g^0/d(1/T) = -\Delta H/2.303R$$

where R is the gas constant. The values of ΔH calculated as shown above for the dinitriles (C_1–C_6) on the liquid phases are listed in Table 2.

The viscosity of the dinitriles at temperatures between 130 and 170°C were calculated according to the following equation (*10, 11*), and the values are listed in Table 3:

$$\log \eta = A + \frac{B}{C + T}$$

A, B, and C are constants, η is the viscosity in centipoise, and T is the absolute temperature.

DISCUSSION

Table 2 indicates that the values of ΔH for each member of the dinitriles become more negative as the percentage of phenyl groups increases. This means that the lowest negative values of ΔH for OV-1 are due to the small tendency for specific interaction with the dinitriles. Substitution of phenyl groups into the methyl silicons increases this tendency. Moreover, Table 1 shows that the order of elution of dinitriles (C_1–C_6) in this series of liquid is mainly affected by their boiling point, but the extent of interaction and the selectivity of these liquid phases toward the dinitriles are in the order

$$\text{OV-25} > \text{OV-11} > \text{OV-3} > \text{OV-1}$$

Table 2 also indicates that ΔH has higher negative values for polyesters and polyglycols than for polysiloxane-type liquid phases. DEGGLU has the highest negative value of ΔH among the polyesters (Fig. 1). The order is

$$\text{DEGGLU} > \text{DEGA} > \text{DEGS} > \text{EGTCP}$$

with a few exceptions in the case of EGTCP. This means that polyesters

TABLE 1

Constants *a* and *b* of the Equation $\log V_g^0 = (a/T) - b$ for Aliphatic Dinitriles in Different Liquid Phases

	Malononitrile		Succinonitrile		Glutronitrile		Adiponitrile		Pimelonitrile		Suberonitrile	
Liquid phase	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
OV-1	1277	2.02	1639	2.68	1503	2.20	2298	3.86	2635	4.43	2820	4.63
OV-3	1435	2.15	2108	3.43	2200	3.50	2396	3.68	2662	4.09	2916	4.49
OV-11	1649	2.43	2170	3.27	2343	3.50	2607	3.84	2867	4.20	2943	4.69
OV-25	1727	2.67	2400	4.00	2357	3.57	2581	3.78	2819	4.14	2941	4.26
PPG(LB-550-x)	3559	7.07	3929	7.54	3956	7.55	3669	6.52	2729	3.90	2139	2.27
Carbowax 600	2436	4.20	3120	5.38	3120	5.38	3224	5.45	3258	5.39	3446	5.79
Carbowax 6000	2493	4.55	2846	5.05	2327	3.68	2856	4.80	3289	5.70	3390	5.87
DEGS	2578	4.04	2251	2.86	2909	4.38	2754	3.82	3263	4.84	3337	4.92
DEGGLU	4583	8.44	3430	5.36	3430	5.36	3740	5.85	3969	6.20	3943	6.05
DEGA	2713	4.24	3127	4.78	3223	4.97	3103	4.47	3463	5.12	3618	5.37
EGTCP	2320		2689	4.17	2526	3.68	2923	4.31	3140	4.58	3326	4.84

TABLE 2

Heat of Solution ($-\Delta H$) of Aliphatic Dinitriles (kcal/mole) in Different Liquid Phases

Liquid phase	Malononitrile	Succinonitrile	Glutronitrile	Adiponitrile	Pimelonitrile	Suberonitrile
OV-1	5.82	7.48	6.86	10.5	12.0	12.9
OV-3	6.54	9.61	10.0	10.9	12.0	13.3
OV-11	7.52	9.90	10.7	11.9	13.1	13.4
OV-25	7.88	11.3	10.8	11.8	12.9	13.4
PPG(LB-550-x)	16.2	17.9	18.0	16.7	12.5	13.4
Carbowax 600	11.1	14.2	14.2	14.7	14.9	15.7
Carbowax 6000	11.4	13.0	10.6	13.0	15.0	15.5
DEGS	11.8	10.3	13.3	12.6	14.9	15.2
DEGGLU	20.9	15.6	15.6	17.1	18.1	18.0
DEGA	12.4	14.3	14.7	14.2	15.8	16.5
EGTCP	10.6	12.3	11.5	13.3	14.3	15.2

TABLE 3

Viscosity, η, of Aliphatic Dinitriles (centipoise) at Different Temperatures

Compound	170°C	160°C	150°C	140°C	130°C
Glutronitrile	0.8340	0.8937	0.9060	1.1044	1.1139
Adiponitrile	0.8975	0.9033	1.103	1.1058	1.1177
Pimelonitrile	0.8918	0.8984	0.9052	1.1038	1.1136
Suberonitrile	0.8828	0.8906	0.8987	0.9068	1.1075

and polyglycols have a greater tendency for specific interaction with the dinitriles than do polysiloxanes.

For polyglycols the values of ΔH (Table 2) decrease in the order

$$\text{PPG} > \text{Carbowax 600} > \text{Carbowax 6000}$$

This order is in agreement with the extent of availability of OH groups in the structure of these liquid phases for hydrogen bonding with the CN groups of the dinitriles.

Viscosity and Specific Retention Volume

The relationship between the viscosity of solutes and their retention volumes has not yet been considered; only the effect of the viscosity of the stationary liquid phases on the column's efficiency have been studied

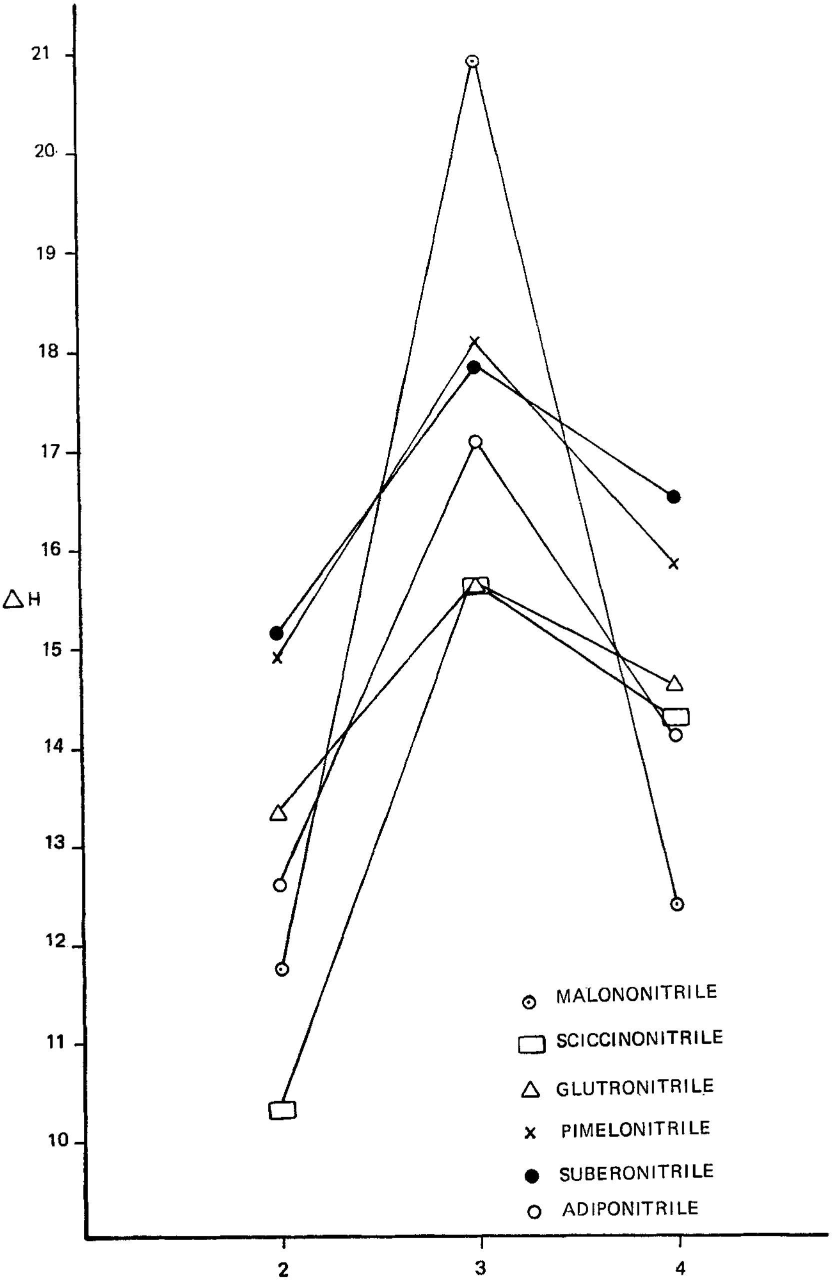

FIG. 1. Plot of ΔH vs number of methylene groups in polyesters.

by a few investigators (*12–14*). This section deals with the relationship between the viscosity η of aliphatic dinitriles and their specific retention volumes V_g^0 and their order of elution. When the log V_g^0 value of each of the dinitriles was plotted versus the log η value (using a 9820A calculator and a 9862A plotter connected to a 9865A cassette memory, Hewlett-Packard) at the temperatures of specific retention volumes, a linear relationship was obtained (Figs. 2 and 3) for which a numerical equation was derived:

$$\log V_g^0 = A + B \log \eta$$

The values of B and A for each of the dinitriles for each of the liquid phases used in this investigation were determined from the slope and the intercept

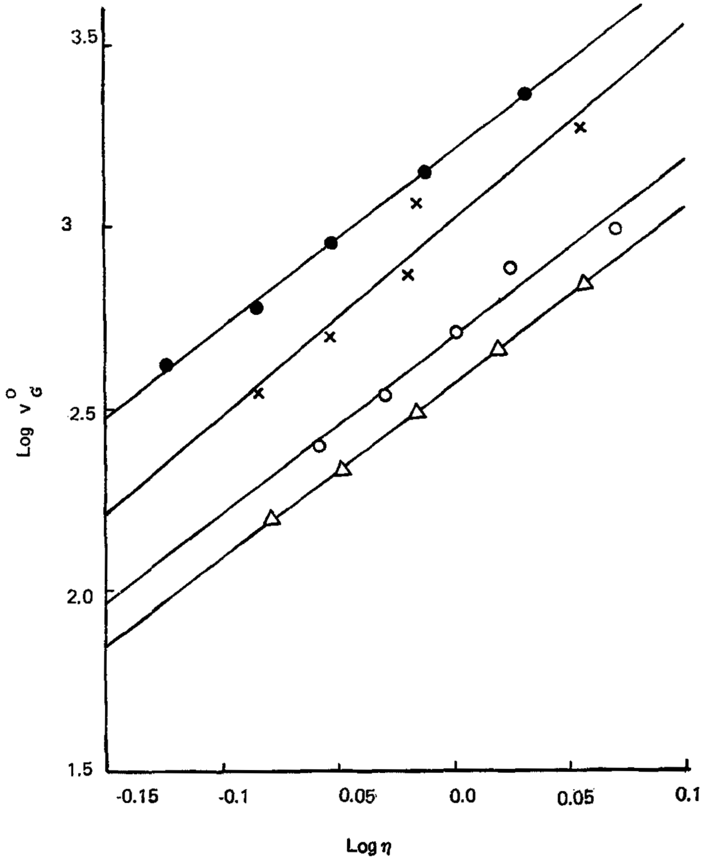

FIG. 2. Plot of log V_g^0 vs log η for polydiethylene glycol succinate (DEGS).

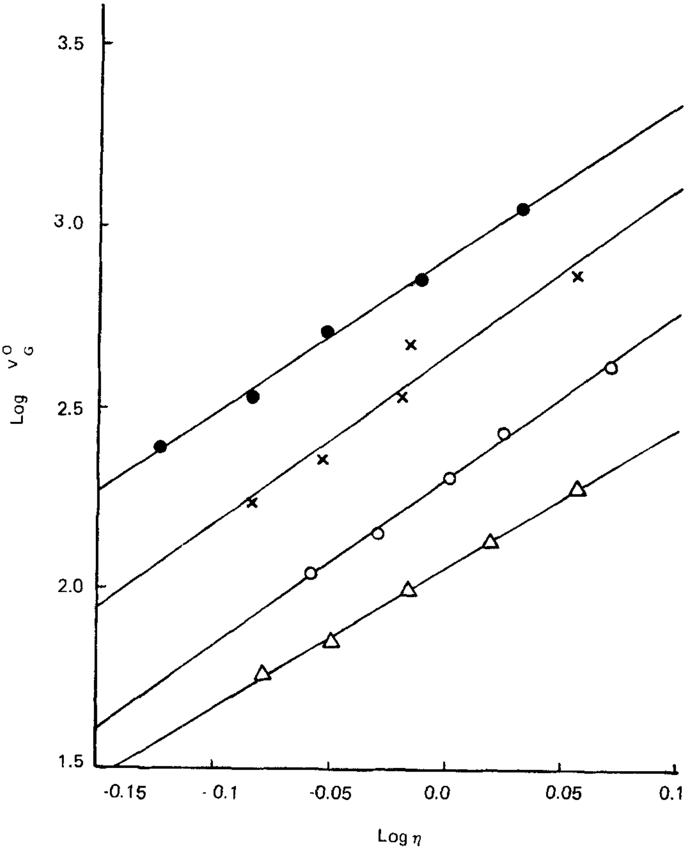

FIG. 3. Plot of log V_g^0 vs log η for 75% phenyl methyl polysiloxane (OV-25).

of these straight lines, respectively, and are tabulated in Table 4. These values of B and A allowed a satisfactory precalculation of V_g^0 for these compounds from their viscosities or vice versa.

Table 4 and Figs. 2 and 3 also indicate that the values of B and A are characteristic of the solvent and solute. Thus the highest values of B were mainly obtained on DEGGLU followed by Carbowax 600, then OV-11 = OV-25. Carbowax 600 has higher values of B than does Carbowax 6000. Furthermore, the values of B did not change systematically with the carbon number of the aliphatic dinitriles; that is, the highest values of B were mainly obtained for pimelonitrile followed by adi-

TABLE 4

Constants *A* and *B* of the Equation $\log V_g^0 = \mathrm{A} + \mathrm{B} \log \eta$ for Aliphatic Dinitriles in Different Liquid Phases

	Glutronitrile		Adiponitrile		Pimelonitrile		Suberonitrile	
Liquid phase	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
OV-3	1.76	3.63	1.99	4.26	2.33	4.35	2.63	4.24
OV-11	2.09	3.86	2.32	4.60	2.69	4.63	3.01	4.88
OV-25	2.06	3.89	2.30	4.60	2.64	4.64	2.91	4.28
DEGS	2.57	4.80	2.69	4.85	3.01	5.34	3.21	4.84
DEGGLU	2.69	3.21	3.01	7.37	3.45	8.62	3.56	5.83
DEGA	2.73	5.33	2.88	5.99	3.21	5.71	3.44	5.27
EGTCP	2.35	4.17	2.60	5.18	2.98	5.14	3.27	4.85
Carbowax 600	2.06	5.14	2.17	5.71	2.45	5.30	2.61	5.02
Carbowax 6000	1.88	3.62	1.96	4.79	2.22	5.03	2.39	5.05

ponitrile. Glutronitrile has the lowest values of *B* for most of the liquid phases used.

These results imply the presence of selective interactions between aliphatic dinitriles and the stationary liquid phases and are in good agreement with the ΔH values (Table 2 and Fig. 1).

Acknowledgments

The authors are grateful to the Head of the Chemistry Department, College of Science, and the University of Baghdad for providing the facilities for carrying out this work.

REFERENCES

1. G. A. Dardenne and M. S. Ey. M. Malier, *J. Chromatogr.*, *47*, 176–181 (1970).
2. A. A. Hassan Kadhem, M.Sci. Thesis, University of Baghdad, September 1976.
3. I. Hor Lysyj, *J. Anal. Chem. 32*, 771 (1960).
4. M. Taramasse and A. Guerra, *J. Gas Chromatogr.*, p. 138 (April 1965).
5. E. Mugnaini and G. Gambelli, *Chim. Ind.* (*Milan*), *45*(1), 44–45 (1963).
6. A. B. Littlewood, C. S. G. Phillips, and D. T. Price, *J. Chem. Soc.*, *1955*, 1480.
7. V. Kubecova, J. Novak, and J. Janak, *J. Chromatogr.*, *110*, 63–72 (1975).
8. V. R. Choudhary and P. G. Menon, *Ibid.*, *116*, 431 (1976).
9. A. E. Habboush and K. A. B. Najm, *Ibid.*, *30*, 161 (1977).
10. F. Gutmann and L. M. Simmons, *J. Appl. Phys.*, *23*, 977 (1952).
11. A. L. Woodman, W. J. Murbach, and M. H. Kaufman, *J. Phys. Chem.*, *64*, 658 (1960).

12. J. J. Van Deemter, F. J. Zniderweg, and A. Klinkenberg, *Chem. Eng. Sci.*, *5*, 271 (1956).

13. J. C. Giddings, *Anal. Chem.*, *35*, 439 (1963).

14. W. E. Harris and H. W. Habgood, *Talanta*, *11*, 115 (1964).

Received by editor September 6, 1978