

Solvent Polarity as a Function of R_f in Thin-Layer Chromatography of Selected Nitro Functions

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Abstract

Solvent polarities have been related to the R_f values of various nitro compounds as linear functions in different solvents. Such relations may prove useful in the determination of the polarity of a solvent or in the evaluation of the polarities of mixed solvents.

Introduction

Solvent polarity has been measured by various methods including kinetics (1), thermodynamics (2), and spectroscopy (3). There are many well-known polarity scales: $E_T[30]$ (4), Kawasawa Z scale (Z) (5), Gutmann Acceptor No. (AN) (6), Gutmann Donor No. (DN) (7), and Kamlet TAfts (π^*) (8).

However, there is still a need for a simple method to evaluate solvent polarity. We determined the R_f values of nitro compounds in various solvents by thin-layer chromatography (TLC). The various linear functions we obtained can be used to predict solvent polarities that are unknown or to evaluate solvent polarities in a mixture. In this communication, we report our results for single solvent system. A similar approach has been reported in the literature (9–11).

Experimental

Silica gel G (for TLC) was obtained from Merck (India). The nitro compounds were obtained from BDH, E. Merck, or Fluka. All solvents were analytical-reagent grade and were obtained from BDH, E. Merck, or Kochlight. The solvents were used without further purification. Most of the solvents were dried over 4 Å molecular sieve and were not evaluated for traces of water because traces of water would not have a significant effect on R_f . This supposition was later confirmed by the linear relationship obtained.

For each development, the TLC tank was covered with a

greased glass lid that was removed only when the development was complete.

The TLC plates were prepared on microscopic slides. Care was taken to ensure that layers were as uniform as possible. To achieve this end, the microscopic slides were suspended in a slurry of silica gel G that was prepared by adding 40 mL water to 60 g dry gel. The mixture was agitated continuously with an electrical shaker to maintain uniformity of the slurry. All slides were removed after 30 s. No binder was used. Nitroanilines could be detected by their intense yellow–red color.

For each nitroaniline, solutions were prepared by dissolving 2 g aniline in ethanol to give 100 mL of solution. The plates were spotted with a fine glass capillary. The drop size was not measured because R_f values are not dependent on sample concentration. All experiments were carried out at 30°C. The plates were spotted with various nitro compounds and run in different solvents in closed glass chambers.

Lotus was used to perform regression analysis of the data and to obtain the equations shown in Table I.

Results and Discussion

The nitro compounds used in the study are listed in Table I and the solvents are listed in Table II. For each nitro compound in different solvents, an equation of the form $R_f = m [\log E_T(30) - c]$ was obtained, where m and c are the slope and intercept, respectively.

Table I. Regression Equations Used to Evaluate the Polarity Values

Compound	Regression equations
<i>m</i> -Nitroaniline	$R_f = 8.49 (\log E_T [30] - 1.50)$
<i>o</i> -Nitroaniline	$R_f = 10.05 (\log E_T [30] - 1.51)$
<i>p</i> -Nitroaniline	$R_f = 10.11 (\log E_T [30] - 1.51)$
<i>o</i> -Nitrophenol	$R_f = 26.45 (\log E_T [30] - 1.55)$
Picric acid	$R_f = 10.79 (\log E_T [30] - 1.54)$

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Figures 1 and 2 show two such plots. The various equations obtained for different nitro compounds are shown in Table I. The solvent polarity values obtained with this method and the standard $E_T[30]$ values are shown in Table II. For the experimental evaluation of $E_T[30]$, these values were read directly from the plot at the respective R_f values obtained experimentally and then compared with the established values. We also evalu-

ated the average percent error (average of all errors, which is defined here as the difference between the solvent polarity values obtained by our method and the standard $E_T[30]$ values); these values are appended in Table II. Regression equations were used to evaluate the values.

In some cases, the average percent error obtained with this method was slightly high, but the method is simple and the sys-

Table II. Values of $E_T[30]$ Obtained for Each Solvent

No.	Solvent	Standard $E_T[30]$	Values of $E_T[30]$ obtained for each solvent				
			ONA	PNA	MNA	ONP	PAC
1	Methanol	55.5	40.05	38.41	39.10	38.37	41.99
2	Carbon tetrachloride	32.5	32.33	34.10	33.19	37.87	35.02
3	Acetone	42.2	38.87	38.59	40.19	38.84	41.47
4	1,2-Dichloroethane	41.9	38.14	38.41	36.19	38.98	35.62
5	Dimethyl formamide	43.8	38.35	38.50	40.65	38.07	43.25
6	Chloroform	39.1	35.45	37.89	36.85	38.67	35.02
7	Hexane	30.9	31.63	32.42	32.59	37.09	35.02
8	Benzene	34.5	35.26	36.52	34.89	38.24	35.02
9	Acetic acid	51.7	40.05	37.89	39.46	37.38	41.47
10	Acetonitrile	46.0	40.16	39.84	40.37	38.71	42.53
11	Ethyl acetate	38.1	39.94	40.76	40.74	38.84	37.16
12	Cyclohexanol	46.3	40.93	40.76	40.19	39.18	39.17
13	Acetophenone	41.3	41.26	40.76	40.00	38.77	36.84
14	Diethyl ether	34.6	40.82	40.76	40.92	39.18	35.02
15	Methylacetate	40.0	41.49	40.76	40.92	39.18	42.71
16	DMSO	45.0	40.82	39.48	40.92	39.18	43.25
17	Dichloromethane	41.1	39.19	40.21	37.70	39.05	35.47
18	Cyclohexanone	39.8	41.49	39.30	40.92	38.51	40.51
Average % error			1.17	1.29	1.23	1.47	1.12

*Abbreviations: ONA, *o*-nitroaniline; PNA, *p*-nitroaniline; MNA, *m*-nitroaniline; ONP, *o*-nitrophenol; PAC, picric acid.

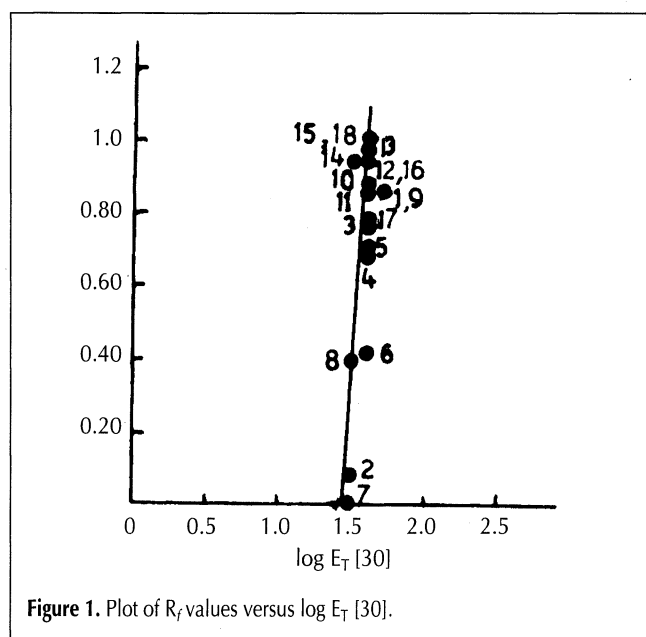


Figure 1. Plot of R_f values versus $\log E_T[30]$.

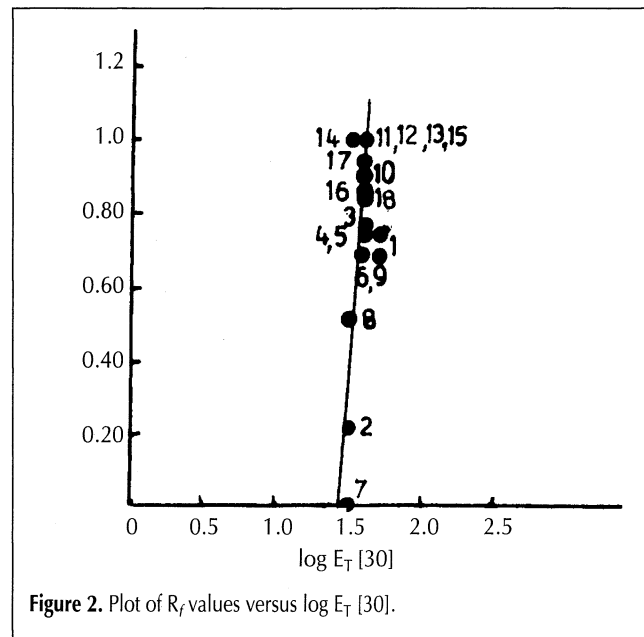


Figure 2. Plot of R_f values versus $\log E_T[30]$.

tems (solvents) involved were complex.

As mentioned previously, solvent polarity is an important parameter and simple methods should be available to approximate the value. Similar relationships can also be used to predict the R_f values of single compounds in various solvents.

This method will be best suited for mixed solvents where the solvent polarities may not be easy to obtain with conventional, often time-consuming methodology.

Conclusion

The linear relationship between R_f and solvent polarity is of fundamental importance. These results confirm earlier studies and show that solvent polarity has a profound (often dominating) effect on the chromatographic process.

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