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GAS CHROMATOGRAPHIC BEHAVIOUR OF C1–C4 ALIPHATIC AMIDES AND THEIR N-METHYL AND N,N-DIMETHYL DERIVATIVES ON POROUS POLYMERS OF THE PORAPAK TYPE

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SUMMARY

Aliphatic amides can be analyzed, without any preliminary treatment, by gas chromatography on porous copolymers of the Porapak type. On all of the copolymers studied, amides gave symmetrical chromatographic peaks. The best separation was achieved on Porapak N; all unsubstituted, N-methyl and N,N-dimethylamides of formic, acetic, propionic and butyric acids were separated, except for the pair N-methyl- and N,N-dimethylformamide, which were separated on Porapak Q and T. The sorption of amides on Porapak P, Q, N, R and S and on Synachrom is due mainly to non-specific interactions. Only Porapak T displays appreciable polarity; the order of retention of amides suggests that Porapak T is both an electron donor and, to a lesser extent, an electron acceptor type of adsorbent. The differences in the retentions of amides on Porapak P and Q are in accordance with the difference in the specific surface areas of these sorbents, but the sorption enthalpies are almost identical. The solute–sorbent interaction is of the same nature in both instances, regardless of an order of magnitude difference in the specific surface areas. The excellent sorption properties of Porapaks permitted the reliable determination of the response factors of amides in their detection with flame ionization and thermal conductivity detectors.

INTRODUCTION

Amides are among the most polar organic compounds. Owing to the high propensity of the amide group to undergo hydrogen bonding, the molecules of amides are strongly associated with one another so that even amides of low molecular weight display very low volatilities. For instance, the simplest aliphatic amide, formamide, has been used as a gas chromatographic (GC) stationary phase[1].

In extremely dilute solutions of amides in non-polar solvents, the intermolecular association due to hydrogen bonding is almost zero and the volatilities of the dissolved amides are markedly increased (large positive deviation from Raoult's law). Hence, the GC of amides is feasible with the use of non-polar stationary phases, but the application of conventional GLC packings for this purpose is difficult owing

to the strong adsorption of amides on the surface of the support. The extent of peak tailing is usually intolerable even with the use of very inactive supports.

It follows that non-polar porous organic polymers can be very advantageous sorbents for the GC of free amides. Although the thermodynamic properties of a solute molecule adsorbed on a solid surface are different in many respects from those of the molecule dissolved in a liquid, the effect of the supression of the association of solute molecules applies in both instances.

Aliphatic amides have been analyzed by GC on a mixed stationary phase of orthophosphoric acid and poly(ethylene glycol succinate) deposited on Chromosorb W[2]. At the temperature employed (205°C), the amides were dehydrated to the corresponding nitriles on the stationary phase. A disadvantage of this method was that the conversion was incomplete. Metcalfe et al.[3] chromatographed aliphatic amides at 220°C on Apiezon L on Chromosorb W treated with sodium hydroxide. O'Donnell and Mann[4] separated lower aliphatic amides at 220°C on Dowfax 10 plus sodium hydroxide deposited on Chromosorb W. VandenHeuvel et al.[5] chromatographed amides after their conversion into more volatile fluoro derivatives.

Yasuda and Nakashima[6] used Porapak Q for the GC of aliphatic amides at 230°C; N-methyl derivatives of the amides were converted into nitriles on a pre-column with orthophosphoric acid prior to the GC analysis proper. Chromosorb 101 was employed by Nakagawa et al.[7] in the temperature-programmed GC of a mixture of C_2–C_4 fatty acids and their amides.

In this paper, we present the results of a systematic investigation of the chromatographic behaviour of C_1–C_4 aliphatic amides and their N-methyl and N,N-dimethyl derivatives on Porapak P ,Q, N, R, S and T and on Synachrom E-5 (ref. 8).

EXPERIMENTAL

Chemicals

Solutes. Formamide and N,N-dimethylformamide were commercial products (Lachema, Brno, Czechoslovakia), purified by distillation. The unsubstituted, N-methyl and N,N-dimethylamides of acetic, propionic and butyric acids were synthesized from the acids by esterification with ethanol and subsequent shaking of the esters with ammonia solution, methylamine and dimethylamine, respectively[9]. The isolation of pure amides from the reaction mixture was carried out by preparative GC on a Perkin-Elmer 900 (Norwalk, Conn., U.S.A.) gas chromatograph provided with an auxiliary preparative unit, employing a 6-m stainless-steel column, packed with Porapak Q, 80–100 mesh, maintained at 185°C. C_6–C_{10}, C_{14}, C_{16} and C_{18} *n*-alkanes (BDH, Poole, Great Britain) were used as reference solute compounds.

Chromatographic materials. The Porapaks employed were products of Waters Ass., Framingham, Mass., U.S.A., and Synachrom E-5 was obtained from the Research Institute of Plastics and Lacquers, Pardubice, Czechoslovakia. The batch numbers, particle sizes and specific surface areas of the polymers are given in Table I.

Instruments and procedures

Measurement of retention data. The measurement of the retention characterics of amides was carried out on a Chrom 2 gas chromatograph (Laboratorní Přístroje, Prague, Czechoslovakia) equipped with a flame ionization detector (FID),

TABLE I

SPECIFICATIONS OF THE SORBENTS INVESTIGATED

Sorbent	Particle size (mesh)	Batch number	Specific surface area (m^2/g)
Porapak P	80–100	596	68
Q	100–120	594	Not measured
	100–120	558	654
	80–100	638	Not measured
R	100–120	620	636
S	80–100	684	591
T	80–100	691	195
N	100–120	500	503
Synachrom E-5	60–70	---	290

using nitrogen as the carrier gas. The experiments were designed so as to provide the data necessary for calculating the specific retention volumes. The flow-rate of the carrier gas was measured with a differential manometer showing the pressure drop across a capillary, and the column inlet pressure was measured with a mercury manometer. Both devices were installed ahead of the sample inlet port in the carrier gas line. The flow-rate of the carrier gas was maintained within 0.7–1.0 ml/sec. U-shaped 60- or 30-cm (depending on the sorption capacity of the given material) brass columns of 7 mm I.D. were employed. All of the polymers investigated were purged with nitrogen for 20 h at 170°C prior to the measurements proper.

The amides were dissolved in acetone, and about 5-μl portions of the solutions were injected into the gas chromatograph. The charges contained about 1 μg of each amide, except for formamide, the amount of which had to be about ten times greater owing to the lower sensitivity of the FID towards this compound. All of the measurements were performed under isothermal conditions at several temperatures within the range 135–185°C. Methane was employed as the marker of the column hold-up time. Some examples of the separation of amides on Porapaks were provided on a Hewlett-Packard 402 gas chromatograph (cf., measurement of FID response factors).

Measurement of response factors. The FID and thermal conductivity detector (TCD) response factors of amides were measured on a Hewlett-Packard 402 (Avondale, Pa., U.S.A.) and a Perkin-Elmer 900 gas chromatograph, respectively. In the work with the FID, the analyses were carried out on a 1 m × 6 mm I.D. glass column with Porapak P at 170°C. The operating conditions of the detector were as follows: carrier gas (nitrogen) flow-rate, 42–72 ml/min; hydrogen flow-rate, 109–125 ml/min; air flow-rate, 600 ml/min; detector temperature, 170°C; and sensitivity attenuation, 1/400–1/800. A disc integrator (Disk Instruments, Santa Ana, Calif., U.S.A.), built-in in the recorder, was employed for the evaluation of the peak areas. In the work with the katharometer, the samples were chromatographed on a 90 cm × 3.1 mm I.D. stainless-steel column with Porapak Q at 170°C, using hydrogen as the carrier gas. The operating conditions were as follows: carrier gas flow-rate, 19.2 ml/min; katharometer bridge current, 275 mA; detector temperature, 220°C; and full detector sensitivity. The chromatograms were recorded with a Honeywell-Brown (Philadelphia, Pa., U.S.A.) recorder at a chart speed of 0.2 in./min, and the

TABLE II

CONSTANTS a AND b OF THE EQUATION LOG $V_g = (a/T) - b$ FOR AMIDES ON PORAPAKS AND SYNACHROM

Solute*	n**	Sorbent												
		P		Q		N		R		S		T		SCH	
		a	b	a	b	a	b	a	b	a	b	a	b	a	b
1A	0	28.65	5.83	22.52	3.97	27.17	4.53	32.09	6.01	41.33	8.04	35.65	6.31	32.69	5.99
2A	1	31.61	6.33	29.13	5.10	29.65	4.81	43.21	8.25	39.21	7.26	43.23	7.80	42.94	7.90
3A	2	32.95	6.39	33.13	5.69	32.90	5.24	45.15	8.39	41.91	7.55	45.58	8.16	47.69	8.70
4A	3	36.05	6.83	36.51	6.10	37.90	6.01	49.67	9.07	45.84	8.09	48.77	8.65	47.41	8.34
1B	0	30.14	5.99	27.43	4.82	30.59	5.12	37.64	7.05	44.82	8.57	35.31	6.23	42.03	7.86
2B	1	33.33	6.57	30.85	5.31	32.41	5.31	44.15	8.30	41.51	7.58	39.08	6.94	49.62	9.33
3B	2	36.51	7.09	34.16	5.80	36.10	5.89	46.61	8.60	43.85	7.84	40.73	7.17	51.44	9.50
4B	3	37.79	7.13	38.39	6.44	42.41	6.97	53.70	9.88	47.06	8.25	43.61	7.60	51.25	9.15
1C	0	29.52	5.84	29.12	5.14	29.76	4.97	36.33	6.79	31.36	5.54	34.38	6.23	37.47	6.84
2C	1	32.79	6.35	34.37	5.98	36.48	6.17	47.64	9.00	42.15	7.65	37.11	6.62	40.56	7.19
3C	2	36.39	6.96	35.41	5.96	36.79	5.99	50.33	9.35	42.33	7.44	39.85	7.10	43.62	7.65
4C	3	39.83	7.50	38.67	6.39	41.28	6.69	55.33	10.18	48.58	8.52	42.73	7.56	46.81	8.09

* 1, 2, 3 and 4 represent formamide, acetamide, propionamide and butyramide, and A, B and C designate unsubstituted, N-methyl- and N,N-dimethyl-amides, respectively.

** In $C_nH_{2n+1}COR$, where R $= -NH_2$, $-NHCH_3$ or $-N(CH_3)_2$.

peak areas were measured with a planimeter. In both instances, defined volumes of solutions of known concentrations of the individual amides in acetone were introduced into the gas chromatograph, employing the on-column injection method. A Hamilton 701 N syringe (Micromesure N.V., The Hague, The Netherlands) and a Zimmermann (Leipzig, G.D.R.) 40-μl syringe were used in the work with the FID and TCD, respectively. The concentrations of the amides in the model solutions were about 1 % (w/v), except for formamide with the FID, where the concentration was about 10 %. After each amide sample charge or after a series of three charges, defined amounts of C_8, C_9 and C_{10} n-alkanes (reference compounds) were injected and their chromatograms run under the same conditions.

RESULTS AND DISCUSSION

Retention characteristics

All of the retention data measured for the individual amides and reference hydrocarbons at different temperatures were expressed in the form of the absolute specific retention volumes[10], V_g, and these values were further processed by linear regression so as to obtain the constants a and b of the equation

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

where T is the absolute temperature of the system. The results are given in Table II.

The constant a is related to the standard molar enthalpy of sorption, ΔH^0, by the equation

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

where R is the gas constant. The values of ΔH^0 calculated as shown above for all of the amides on Porapak P and Q are listed in Table III. It is interesting that the ΔH^0 values on Porapak P and Q do not differ appreciably, although there is about an order of magnitude difference in the specific surface areas and the sorption capacities of these materials. Fig. 1 shows the temperature dependence of log V_g for acetamide and N,N-dimethylacetamide measured on Porapak P (Fig. 1a) and Porapak Q (Fig. 1b). The similarity of the ΔH^0 values and the difference in the sorption capacity are apparent from the slopes and positions of the lines for Porapak P and Q. Hence it follows that the solute–sorbent interactions are of the same nature with both types of Porapak, the difference in the sorption capacity being given merely by the difference in the entropy of sorption.

Table IV gives the Kováts retention indices, I_{170}, of the amides on the Porapaks at 170°C. The actual separation in the systems studied is demonstrated by the chromatograms in Fig. 2. It can be seen that the best separation is achieved on Porapak N. The pair N-methyl and N,N-dimethylformamide, which is unresolved on Porapak N, can be separated on Porapak Q and T. The sequence of the retention indices reflects the selectivity of the individual types of Porapak to the amide group. Thus, when considering propionamide and N,N-dimethylpropionamide, for instance, the orders of the selectivity towards the –$CONH_2$ and –$CON=$ groups are Q > S > R > P > N > SCH > T and S > R > Q > N > P > SCH > T, respectively. Porapak

TABLE III

STANDARD ENTHALPIES OF SORPTION ($-\Delta H^{\circ}$) OF AMIDES ON PORAPAK P AND Q

β is the 95% interval of confidence.

| Solute[*]	Porapak P		Porapak Q	
	$-\Delta H^{\circ}$ (kcal/mole)	β (kcal/mole)	$-\Delta H^{\circ}$ (kcal/mole)	β (kcal/mole)
1A	13.1	11.9–14.3	10.4	9.2–11.4
2A	14.5	13.3–15.7	13.3	12.3–14.4
3A	15.1	14.1–16.1	15.2	14.2–16.1
4A	16.5	15.2–17.8	16.7	15.3–18.1
1B	13.8	12.5–15.1	12.5	11.7–13.4
2B	15.2	14.5–16.0	14.1	13.2–15.0
3B	16.7	15.7–17.7	15.6	14.2–17.0
4B	17.3	16.3–18.3	17.6	15.6–19.5
1C	13.5	12.6–14.5	13.3	11.6–15.1
2C	15.0	13.6–16.4	15.7	14.3–17.2
3C	16.7	15.4–17.9	16.2	14.1–18.3
4C	18.2	16.9–19.5	18.0	15.4–20.0

[*] For solutes, see footnote to Table II.
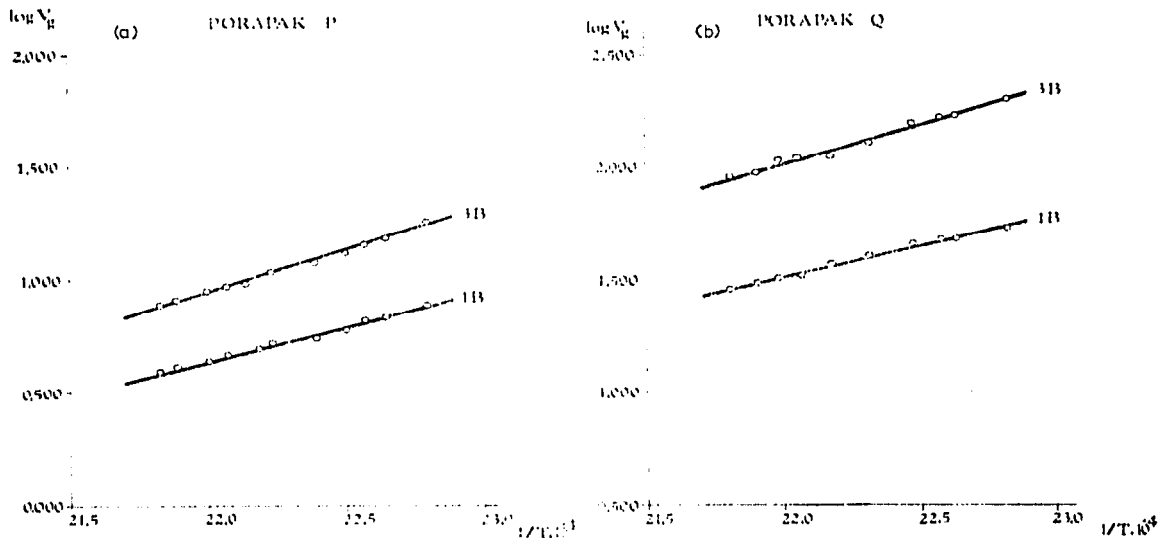
Fig. 1. Temperature dependence of log V_g for acetamide and N,N-dimethylacetamide measured on (a) Porapak P and (b) Porapak Q.

Q, R and S are virtually non-selective, a slight selectivity can be observed with Porapak P, N and with Synachrom (SCH), and the most pronounced selectivity is shown by Porapak T. The differences between the largest and the smallest values of the retention index of propionamide and N,N-dimethylpropionamide are 452 and 295, respectively. Provided that the least selective Porapaks are virtually non-selective, these two differences represent the selectivity of Porapak T towards the $-CONH_2$ and $-CON=$

TABLE IV

KOVÁTS RETENTION INDICES OF AMIDES ON PORAPAKS AND SYNACHROM AT 170 °C

Solute*	I_{170}						
	P	Q	N	R	S	T	SCH
1A	758	654	756	687	666	1140	755
2A	816	744	837	760	755	1221	875
3A	898	834	922	848	841	1286	960
4A	988	936	1020	947	940	1371	1049
1B	818	718	806	750	740	1142	823
2B	865	796	871	808	809	1196	902
3B	936	872	942	884	884	1247	971
4B	1022	966	1044	977	976	1328	1065
1C	821	742	811	742	737	1064	824
2C	899	834	895	836	829	1149	920
3C	973	911	965	910	903	1198	992
4C	1052	998	1051	998	994	1271	1078

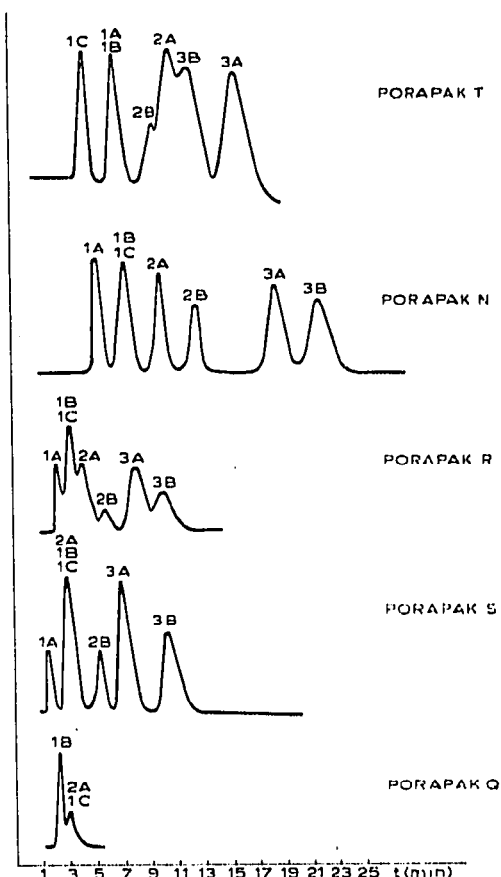* For solutes, see footnote to Table II.

Fig. 2. Chromatograms of amides on Porapaks at 170 °C. For the designations of the peaks, see footnote to Table II.

groups, respectively. This indicates that Porapak T is both an electron donor and an electron acceptor type of adsorbent, but the electron donor character predominates. Note that while the retention of all of the amides on Porapak T increases with increasing length of the hydrocarbon chain attached to the CO group, the methylation of the NH_2 group results in a decrease in retention.

Response factors

Both the FID and TCD response factors of the amides (i) were expressed in the form of the relative molar response, $RMR_{i,r}$, employing n-decane and n-octane as reference compounds (r), respectively. The results were calculated by means of the equation

$$RMR_{i,r} = (A_i/N_i)/(A_r/N_r)$$

where A_i and A_r are the peak areas corresponding to N_i and N_r moles of the amide and the reference compound; N_i and N_r were introduced in separate charges into the gas chromatograph. The results, representing averages of three determinations, are given in Table V, where ΣC_{eff} is the number of effective carbon atoms[11]. The latter quantity was calculated from the equation[12]

$$RMR_{i,r} = (\Sigma C_{eff})_i/(\Sigma C_{eff})_r$$

where, in this work, $(\Sigma C_{eff})_r = 10$ (carbon number of decane).

With both the FID and TCD, the $RMR_{i,r}$ value is linearly proportional to the methylene carbon number within a homologous series of amides, as shown in Figs. 3

TABLE V

RELATIVE MOLAR RESPONSES ($RMR_{i,r}$) OF AMIDES IN THEIR DETECTION WITH THE FLAME IONIZATION DETECTOR AND KATHAROMETER

$(\Sigma C_{eff})_i$ is the sum of the effective carbon atoms of the solute compound (i) in its detection with the FID.

Solute*	n**	Mol. wt.	FID		TCD
			$RMR_{i,r}$	$(\Sigma C_{eff})_i$	$RMR_{i,r}$
1A	0	45.04	0.0030	0.03	0.4585
2A	1	59.07	0.0798	0.80	0.5041
3A	2	73.09	0.1555	1.56	---
4A	3	87.12	0.2358	2.36	0.5906
1B	0	59.07	0.0765	0.76	0.4781
2B	1	73.09	0.1566	1.57	0.5259
3B	2	87.12	0.2360	2.36	0.5772
4B	3	101.15	0.3214	3.71	0.6212
1C	0	73.09	0.1568	1.57	0.5069
2C	1	87.12	0.2299	2.30	0.5694
3C	2	101.15	0.3252	3.25	0.5903
4C	3	115.18	0.4144	4.14	0.6556

* For solutes, see footnote to Table II.
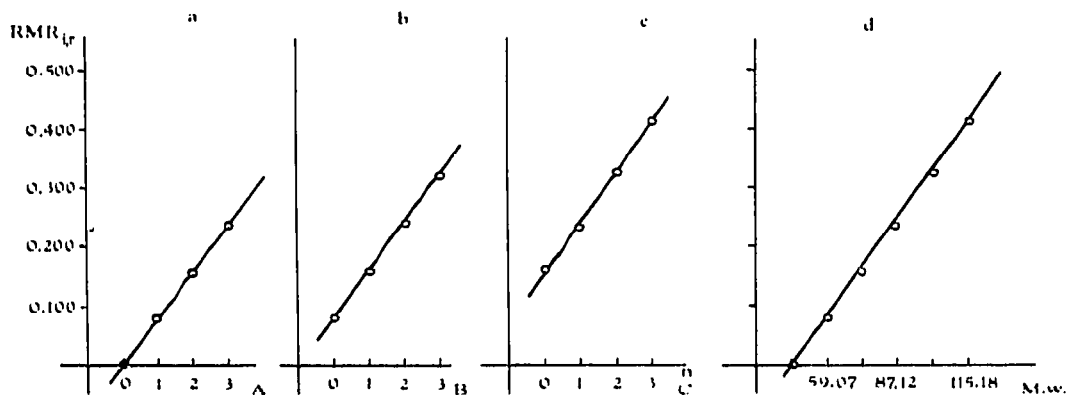** In $C_nH_{2n+1}COR$, where $R = -NH_2$, $-NHCH_3$ or $-N(CH_3)_2$.

Fig. 3. Dependence of $RMR_{i,r}$ on the methylene carbon number for (a) unsubstituted, (b) N-methyl- and (c) N,N-dimethylamides and (d) on molecular weight for all of the amides in their detection with the FID.
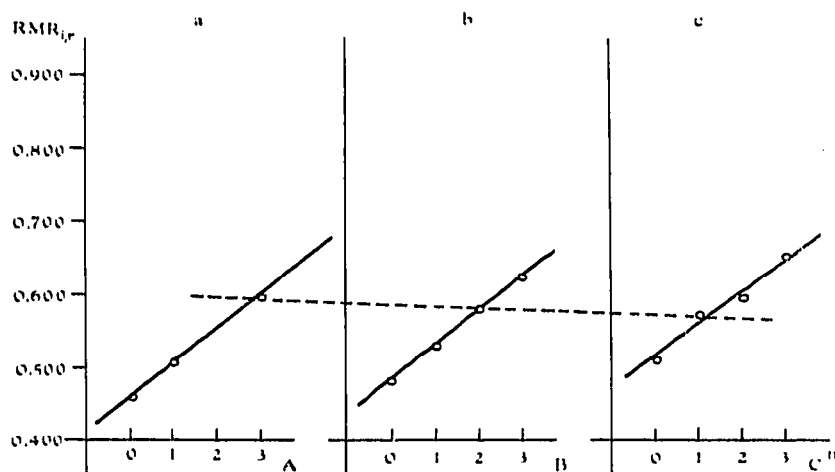

Fig. 4. Dependence of $RMR_{i,r}$ on the methylene carbon number for (a) unsubstituted, (b) N-methyl- and (c) N,N-dimethylamides in their detection with the TCD.

and 4. However, as concerns the dependence of the $RMR_{i,r}$ value on the structure of the amide molecule is concerned, the FID and TCD give different relationships. With the FID, the contribution of a CH_2 group to the $RMR_{i,r}$ value is the same, regardless of whether the group is part of the chain bound to the carbonyl group or of the substituted amide group. Thus, the $RMR_{i,r}$ values of all of the unsubstituted, N-methyl- and N,N-dimethylamides actually lie on a single line in the graph of $RMR_{i,r}$ versus methylene carbon number or molecular weight. Note that the line in Fig. 3d crosses the abscissa in the point corresponding to the molecular weight of formamide. The response to the $-CONH_2$, $-CONH-$ and $-CON=$ groups alone is almost zero. With the katharometer, the average contributions of a CH_2 group at the carbonyl and at the amide group to the $RMR_{i,r}$ value are about 0.044 and 0.027, respectively, under the given conditions.

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