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A METHOD FOR CALCULATING CAPACITY FACTORS AT DIFFERENT MOBILE PHASE COMPOSITIONS AND AT DIFFERENT TEMPERATURES FOR MEMBERS OF HOMOLOGOUS SERIES IN REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY. III*

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SUMMARY

The linear dependences of log k' on the carbon chain length, on log(methanol concentration) and on the reciprocal of absolute temperature in reversed-phase high-performance liquid chromatography of homologous series have been used as a basis for deriving equations for calculating the capacity factors of any member of a homologous series at any mobile phase composition and at any temperature. Good agreement was observed between the published and re-calculated data.

INTRODUCTION

The prediction of the liquid chromatographic behaviour of a solute under varying chromatographic conditions is of a great importance, as it enables the chromatographer to choose a suitable mobile phase composition and/or temperature for achieving optimal separations according to calculated values without performing a complicated optimization of the chromatographic process. The unique properties of homologous series offer great advantages for studying the relationship between the retention of a compound in the column and chromatographic conditions such as temperature, mobile phase composition and structure of the molecules, especially the carbon chain length.

Some dependences of log k' on carbon number[1–4], temperature[3–5] and mobile phase composition[2,3,6,7] in the reversed-phase liquid chromatography of various homologous series have been published. Equations have also been proposed for calculating the capacity factor of any homologue under identical chromatographic conditions[1] or even at various mobile phase compositions[2].

In this paper we discuss the above-mentioned dependences of log k' with the aim of calculating the retention data of solutes, mostly members of homologous series, at various mobile phase compositions and temperatures.

* For Part II, see ref. 2.

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EXPERIMENTAL

No experiments were carried out. All the data used in the calculations have been published earlier[1–4].

DISCUSSION

In previous papers[1,2] we described the linear dependences of log k' on the alkyl carbon number and on log(methanol concentration) in the mobile phase[2] for N-alkyl phthalimides on both RP-8 and RP-18 columns. According to the data of Grushka *et al.*[3], log k' also depends linearly on the reciprocal of the absolute temperature for different alkyl carbon numbers and for varying concentrations of methanol in the mobile phase for alkylbenzenes on a Hypersil C-18 column. A similar dependence of log k' on $1/T$ was observed by Vigh and Varga-Puchony[4] for *n*-alkanal and 2-alkanone dinitrophenylhydrazones on MicroPak CH-10 and Nucleosil C-18 octadecyl packings with aqueous methanol as the mobile phase.

The dependences of log k' on the alkyl carbon number n, $1/T$ and log c_{methanol} are summarized in Fig. 1. The higher the value of the subscript, the higher is the value of the variable.

The linear dependence of log k' on n (Fig. 1A) was used as a basis for deriving the equation for calculating the capacity factor of any homologue at constant temperature and mobile phase composition[1]:

$$\log k'_{n_3} = \log k'_{n_1} + \log(k'_{n_2}/k'_{n_1}) \cdot \frac{n_3 - n_1}{n_2 - n_1} \qquad (1)$$

where n_1, n_2 and n_3 are carbon numbers; the values of the capacity factors k'_{n_1} and k'_{n_2} have to be measured. The comparison of measured and calculated values of ca-

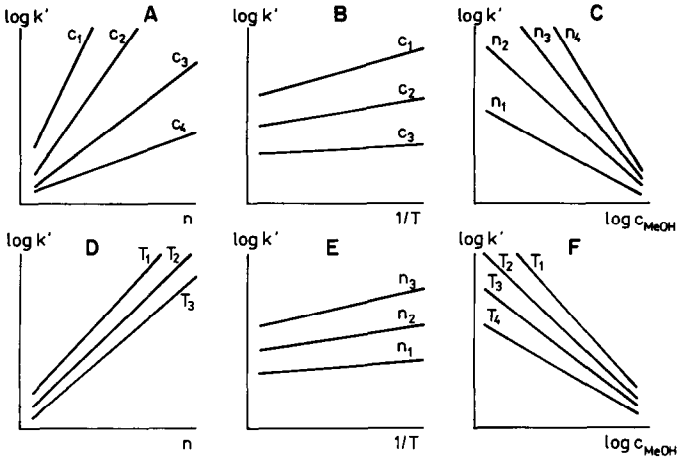

Fig. 1. Dependences of log k' on carbon number (A, D), on reciprocal of absolute temperature (B, E) and on log(methanol concentration) (C, F) for various temperatures T, methanol concentrations c_{methanol} in the mobile phase and carbon chain number n.

pacity factors for N-alkyl phthalimides[1], n-alkanols[4] (see Table I) and alkylbenzenes[3] was excellent; the error did not exceed 2% with the exception of the first non-linear homologues.

Similarly, the linear dependence of log k' on log c_{methanol} (Fig. 1C) can be used for deriving an equation for calculating the capacity factor of a given homologue at any methanol concentration in the mobile phase:

$$\log k'_{c_1} - \log k'_{c_2} = \text{constant}(\log c_2 - \log c_1)$$

and

$$\log k'_{c_3} - \log k'_{c_1} = \text{constant}(\log c_1 - \log c_3)$$

hence

$$\log k'_{c_3} = \log k'_{c_1} + \log (k'_{c_2}/k'_{c_1}) \cdot \frac{\log(c_3/c_1)}{\log(c_2/c_1)} \tag{2}$$

where c_1, c_2 and c_3 indicate methanol concentrations in the mobile phase. For calculating the capacity factor k'_{c_3} it is necessary to measure the capacity factors k'_{c_1} and k'_{c_2} of the compound at methanol concentrations c_1 and c_2, respectively. The important feature of eqn. 2 is that it may be valid not only for members of a homologous series but generally for all chromatographed compounds.

Eqn. 2 was based on the assumption of a linear dependence of log k' on log (methanol concentration) in the mobile phase. It is probable that the concentration of methanol is only an approximation of another thermodynamic quantity (polarity, dielectric constant, etc.) describing the methanol–water system. Whatsoever this quantity may be, its dependence on methanol concentration seems to be at least near to logarithmic. Thus the approximation using concentration is fairly good, as follows from Table II, in which the measured capacity factors of N-alkyl phthalimides on LiChrosorb RP-8[2] are compared with those calculated according to eqn. 2.

A linear dependence of log k' on the reciprocal of absolute temperature (Fig. 1B or E) can be used analogously to obtain an equation for calculating the capacity factor of a compound at the same mobile phase composition at any temperature, k'_{T_3}, assuming we have measured capacity factors k'_{T_1} and k'_{T_2} of the compound at temperatures T_1 and T_2, respectively:

$$\begin{aligned} \log k'_{T_3} &= \log k'_{T_1} + \log (k'_{T_2}/k'_{T_1}) \cdot \frac{1/T_3 - 1/T_1}{1/T_2 - 1/T_1} \\ &= \log k'_{T_1} + \log (k'_{T_2}/k'_{T_1}) \cdot \frac{T_2 (T_1 - T_3)}{T_3 (T_1 - T_2)} \end{aligned} \tag{3}$$

The error seldom exceeds 3%, which is the error of the chromatographic method itself, as can be seen from Table I. Eqn. 3 is also not restricted to members of a homologous series, but it is considered to be valid for all chromatographed compounds.

TABLE I

COMPARISON OF MEASURED CAPACITY FACTORS OF *n*-ALKANOLS ON MICROPAK CH-10[4] (k'_m) WITH VALUES CALCULATED ACCORDING TO EQN. 1 (k'_{n_3}), EQN. 3 (k'_{T_3}) AND EQN. 5 ($k'_{n_3T_3}$)

n-Octanol and *n*-tetradecanol (n_1 = 8 and n_2 = 14) were used as reference compounds at temperatures T_1 = 308.15°K and T_2 = 323.15°K.

Carbon number	*Temperature*										
	30°C (303.15°K)				*35°C (308.15°K)*			*40°C (313.15°K)*			
	k'_m	k'_{n_3}	k'_{T_3}	$k'_{n_3T_3}$	k'_m	k'_{n_3}	$k'_{n_3T_3}$	k'_m	k'_{n_3}	k'_{T_3}	$k'_{n_3T_3}$
6	0.91	0.96	0.93	1.00	0.87	0.93	0.93	0.78	0.83	0.82	0.87
7	1.47	1.48	1.45	1.53	1.34	1.41	1.41	1.26	1.25	1.24	1.30
8	2.29	2.29	2.35	2.35	2.14	–	–	1.89	1.89	1.95	1.95
9	3.54	3.54	3.52	3.62	3.18	3.25	3.25	2.90	2.85	2.88	2.93
10	5.53	5.47	5.71	5.56	5.05	4.93	4.93	4.28	4.31	4.49	4.39
11	8.43	8.45	8.62	8.54	7.59	7.49	7.49	6.41	6.51	6.71	6.59
12	12.91	13.06	13.13	13.13	10.94	11.37	11.37	9.62	9.82	9.89	9.89
13	19.9	20.19	20.42	20.18	17.5	17.26	17.26	14.2	14.83	15.07	14.83
14	31.2	31.20	31.01	31.01	26.2	–	–	22.4	22.40	22.25	22.25
15	48.8	48.22	49.64	47.67	41.9	39.78	39.78	33.4	33.82	35.56	33.38
16	74.3	74.52	73.90	73.26	61.2	60.39	60.39	51.9	51.07	50.99	50.08

We should emphasize the similarity of eqns. 1, 2 and 3, all of which consist of two terms, the first always being the logarithm of one of the two measured capacity factors with subscript n_1, c_1 or T_1, and the second describing the dependence on either carbon number (n), log(methanol concentration (c) or the reciprocal of absolute temperature (T). These terms are again formally analogous (see eqns. 1–3).

By combining dependences of log k' on the carbon number (Fig. 1A) and log k' on log c_{methanol} (Fig. 1C), an equation for calculating the capacity factor $k'_{n_3c_3}$ of a homologue containing n_3 carbon atoms at methanol concentration c_3 has previously been derived[2]:

$$\log k'_{n_3c_3} = \log k'_{n_1c_1} + \frac{n_3 - n_1}{n_2 - n_1} \cdot \log(k'_{n_2c_1}/k'_{n_1c_1}) + \frac{\log(c_3/c_1)}{\log(c_2/c_1)} \cdot \left[\frac{(n_2 - n_3)\log(k'_{n_1c_2}/k'_{n_1c_1}) + (n_3 - n_1)\log(k'_{n_2c_2}/k'_{n_2c_1})}{n_2 - n_1} \right] \quad (4)$$

Its validity has been proved by comparing calculated and measured capacity factors of N-alkyl phthalimides on LiChrosorb RP-8[2].

Analogously, an equation for calculating the capacity factor $k'_{n_3T_3}$ of a homologue containing n_3 carbon atoms at temperature T_3 can be derived by combining the dependences of log k' on the carbon number and log k' on $1/T$ (Figs. 1D and E). According to eqn. 1:

$$\log k'_{n_3T_3} = \log k'_{n_1T_3} + \log(k'_{n_2T_3}/k'_{n_1T_3}) \cdot \frac{n_3 - n_1}{n_2 - n_1}$$

45°C (318.15°K)				*50°C (323.15°K)*			*60°C (333.15°K)*			
k'_m	k'_{n3}	k'_{T3}	k'_{n3T3}	k'_m	k'_{n3}	k'_{n3T3}	k'_m	k'_{n3}	k'_{T3}	k'_{n3T3}
0.74	0.79	0.77	0.81	0.72	0.76	0.76	0.61	0.65	0.64	0.68
1.15	1.18	1.15	1.21	1.07	1.12	1.12	0.95	0.94	0.93	0.97
1.75	1.75	1.79	1.79	1.64	–	–	1.36	1.36	1.39	1.39
2.60	2.60	2.62	2.65	2.39	2.40	2.40	2.02	1.97	2.00	2.00
3.91	3.87	4.00	3.93	3.58	3.53	3.53	2.88	2.85	2.90	2.87
5.75	5.75	5.96	5.83	5.31	5.17	5.17	4.13	4.12	4.26	4.11
8.38	8.55	8.64	8.64	7.46	7.58	7.58	5.99	5.97	5.90	5.91
12.59	12.71	13.04	12.81	11.33	11.12	11.12	8.28	8.64	8.67	8.48
18.9	18.90	19.00	19.00	16.3	–	–	12.50	12.50	12.16	12.16
28.8	28.10	30.33	28.17	26	23.90	23.90	17.6	18.09	19.37	17.46
42.5	41.78	42.73	41.78	36	35.05	35.05	26.6	26.18	25.95	25.06

TABLE II

COMPARISON OF MEASURED[2] AND CALCULATED (EQN. 2) CAPACITY FACTORS FOR N-ALKYL PHTHALIMIDES ON LICHROSORB RP-8 WITH METHANOL–WATER AS THE MOBILE PHASE

Methanol–water ratio	*Phthalimide*									
	N-Butyl		*N-Pentyl*		*N-Hexyl*		*N-Heptyl*		*N-Octyl*	
	k'_{meas}	k'_{calc}	k'_{meas}	k'_{calc}	k'_{meas}	k'_{calc}	k'_{meas}	k'_{calc}	k'_{meas}	k'_{calc}
50:50	12.16	13.00	–	–	–	–	–	–	–	–
55:45	6.94	7.55	12.62	14.04	–	–	–	–	–	–
60:40	4.46	4.59	7.62	7.88	13.00	13.65	–	–	–	–
65:35	2.91*	–	4.63*	–	7.47*	–	12.19*	–	19.47*	–
70:30	1.84	1.91	2.74	2.83	4.14	4.27	6.31	6.51	9.54	9.65
75:25	1.20	1.29	1.69	1.79	2.42	2.54	3.49	3.63	5.01	5.10
80:20	0.86	0.89	1.16	1.17	1.54	1.56	2.09	2.10	2.80	2.80
85:15	0.63*	–	0.78*	–	0.99*	–	1.26*	–	1.60*	–
90:10	–	–	0.56	0.53	0.65	0.64	0.80	0.78	0.96	0.94
95:5	–	–	0.40	0.37	0.44	0.43	0.51	0.49	0.58	0.57
100:0	–	–	–	–	0.32	0.29	0.35	0.32	0.38	0.36

* Used as reference data for k'_{c1} and k'_{c2} (see eqn. 2); c_1 = 65% and c_2 = 85% methanol.

and using eqn. 3 for expressing $k'_{n_1T_3}$ and $k'_{n_2T_3}$,

$$\log k'_{n_1T_3} = \log k'_{n_1T_1} + \log(k'_{n_1T_2}/k'_{n_1T_1}) \cdot \frac{T_2(T_1 - T_3)}{T_3(T_1 - T_2)}$$

and

$$\log k'_{n_2T_3} = \log k'_{n_2T_1} + \log(k'_{n_2T_2}/k'_{n_2T_1}) \cdot \frac{T_2(T_1 - T_3)}{T_3(T_1 - T_2)}$$

we obtain

$$\log k'_{n_3T_3} = \log k'_{n_1T_1} + \frac{n_3 - n_1}{n_2 - n_1} \cdot \log(k'_{n_2T_1}/k'_{n_1T_1}) + \frac{T_2(T_1 - T_3)}{T_3(T_1 - T_2)} \cdot \left[\frac{(n_2 - n_3)\log(k'_{n_1T_2}/k'_{n_1T_1}) + (n_3 - n_1)\log(k'_{n_2T_2}/k'_{n_2T_1})}{n_2 - n_1}\right] \quad (5)$$

Comparison of the capacity factors of *n*-alkanols on MicroPak CH-10 measured by Vigh and Varga-Puchony[4] with those calculated according to eqn. 5 is given in Table I.

The dependence of $\log k'$ on $1/T$ (Fig. 1B) and $\log k'$ on $\log c_{\text{methanol}}$ (Fig. 1F) were used in the same manner to derive an equation for calculating the capacity factor $k'_{c_3T_3}$ of any compound assuming a knowledge of the four capacity factors $k'_{c_1T_1}$, $k'_{c_1T_2}$, $k'_{c_2T_1}$ and $k'_{c_2T_2}$ at two different temperatures T_1 and T_2 at two different methanol concentrations c_1 and c_2, respectively:

$$\log k'_{c_3T_3} = \log k'_{c_1T_1} + \frac{\log(c_3/c_1)}{\log(c_2/c_1)} \cdot \log(k'_{c_2T_1}/k'_{c_1T_1}) + \frac{T_2(T_1 - T_3)}{T_3(T_1 - T_2)} \cdot \left[\frac{\log(c_2/c_3) \cdot \log(k'_{c_1T_2}/k'_{c_1T_1}) + \log(c_3/c_1) \cdot \log(k'_{c_2T_2}/k'_{c_2T_1})}{\log(c_2/c_1)}\right] \quad (6)$$

The agreement of the calculated data with those measured by Grushka *et al.*[3] for alkylbenzenes is fairly good, as can be seen from Table III.

All three eqns. 4, 5 and 6 consist of three terms, the first always being a logarithm of the measured capacity factor with subscript 1. The other two terms describe the dependence of the two variables on one another. These terms again exhibit striking similarity.

On combining all the dependences drawn in Fig. 1, we can derive a general equation for calculating the capacity factor $k'_{n_3c_3T_3}$ of a homologue containing n_3 chain carbon atoms at methanol concentration c_3 and at temperature T_3. According to eqn. 4:

$$\log k'_{n_3c_3T_3} = \log k'_{n_1c_3T_1} + \frac{n_3 - n_1}{n_2 - n_1} \cdot \log(k'_{n_2c_3T_1}/k'_{n_1c_3T_1}) + \frac{T_2(T_1 - T_3)}{T_3(T_1 - T_2)} \cdot \left[\frac{(n_2 - n_3)\log(k'_{n_1c_3T_2}/k'_{n_1c_3T_1}) + (n_3 - n_1)\log(k'_{n_2c_3T_2}/k'_{n_2c_3T_1})}{n_2 - n_1}\right]$$

TABLE III

COMPARISON OF MEASURED CAPACITY FACTORS OF *n*-ALKYLBENZENES[3] (k'_m) WITH VALUES CALCULATED FROM EQN. 6 (k'_6) AND EQN. 7 (k'_7) FOR $c_{methanol}$ = 90%

The reference data used were the measured capacity factors for hexyl- and decylbenzene (n_1 = 6, n_2 = 10) at c_1 = 80% and c_2 = 100% methanol at T_1 = 313.35°K and T_2 = 324.15°K[3].

Carbon number	*Temperature (°C)*														
	29.2			*35.0*			*40.8*			*46.0*			*50.0*		
	k'_m	k'_6	k'_7	k'_m	k'_6	k'_7	k'_m	k'_6	k'_7	k'_m	k'_6	k'_7	k'_m	k'_6	k'_7
1	0.40	0.46	0.46	0.37	0.37	0.38	0.33	0.32	0.34	0.34	0.28	0.30	0.34	0.25	0.27
2	0.58	0.62	0.60	0.48	0.50	0.50	0.46	0.42	0.44	0.44	0.36	0.39	0.42	0.32	0.35
3	0.66	0.75	0.78	0.64	0.63	0.66	0.61	0.56	0.58	0.57	0.49	0.51	0.55	0.45	0.46
4	0.91	0.99	1.02	0.85	0.83	0.86	0.82	0.74	0.75	0.76	0.65	0.66	0.73	0.59	0.60
5	1.22	1.23	1.33	1.12	1.07	1.12	1.06	0.97	0.99	0.99	0.88	0.87	0.94	0.81	0.79
6	1.60	1.73	1.73	1.49	1.46	1.46	1.39	1.29	1.29	1.29	1.14	1.14	1.22	1.03	1.03
7	2.16	2.25	2.26	1.97	1.90	1.91	1.84	1.68	1.69	1.70	1.48	1.49	1.49	1.35	1.36
8	2.88	2.95	2.95	2.61	2.51	2.49	2.44	2.23	2.21	2.19	1.98	1.95	2.04	1.81	1.78
9	3.82	3.89	3.85	3.45	3.29	3.26	3.14	2.91	2.88	2.85	2.57	2.55	2.64	2.34	2.33
10	5.09	5.02	5.02	4.62	4.25	4.25	4.08	3.77	3.77	3.69	3.34	3.34	3.41	3.05	3.05
11	6.75	6.74	6.54	5.96	5.63	5.56	5.34	4.94	4.93	4.74	4.33	4.38	4.43	3.92	4.00
12	9.01	8.98	8.54	7.80	7.41	7.26	7.04	6.43	6.45	6.15	5.58	5.73	5.64	5.02	5.24

and according to eqn. 2:

$$\log k'_{n_1c_3T_1} = \log k'_{n_1c_1T_1} + \log(k'_{n_1c_2T_1}/k'_{n_1c_1T_1}) \cdot \frac{\log(c_3/c_1)}{\log(c_2/c_1)}$$

$$\log k'_{n_2c_3T_1} = \log k'_{n_2c_1T_1} + \log(k'_{n_2c_2T_1}/k'_{n_2c_1T_1}) \cdot \frac{\log(c_3/c_1)}{\log(c_2/c_1)}$$

$$\log k'_{n_1c_3T_2} = \log k'_{n_1c_1T_2} + \log(k'_{n_1c_2T_2}/k'_{n_1c_1T_2}) \cdot \frac{\log(c_3/c_1)}{\log(c_2/c_1)}$$

and

$$\log k'_{n_2c_3T_2} = \log k'_{n_2c_1T_2} + \log(k'_{n_2c_2T_2}/k'_{n_2c_1T_2}) \cdot \frac{\log(c_3/c_1)}{\log(c_2/c_1)}$$

and thus

$$\log k'_{n_3c_3T_3} = \log k'_{n_1c_1T_1} + \frac{n_3 - n_1}{n_2 - n_1} \cdot \log(k'_{n_2c_1T_1}/k'_{n_1c_1T_1}) + \frac{T_2(T_1 - T_3)}{T_3(T_1 - T_2)} \cdot$$

$$\left[\frac{(n_2 - n_3) \log(k'_{n_1c_1T_2}/k'_{n_1c_1T_1}) + (n_3 - n_1) \log(k'_{n_2c_1T_2}/k'_{n_2c_1T_1})}{n_2 - n_1} \right] +$$

$$\frac{\log(c_3/c_1)}{\log(c_2/c_1)} \cdot \left\{ \frac{T_2(T_1 - T_3)}{T_3(T_1 - T_2)} \cdot \right.$$

$$\left[\frac{(n_2 - n_3) \log(k'_{n_1c_2T_2}/k'_{n_1c_1T_2}) + (n_3 - n_1) \log(k'_{n_2c_2T_2}/k'_{n_2c_1T_2})}{n_2 - n_1} \right] +$$

$$\frac{T_1(T_3 - T_2)}{T_3(T_1 - T_2)} \cdot$$

$$\left. \left[\frac{(n_2 - n_3) \log(k'_{n_1c_2T_1}/k'_{n_1c_1T_1}) + (n_3 - n_1) \log(k'_{n_2c_2T_1}/k'_{n_2c_1T_1})}{n_2 - n_1} \right] \right\} \quad (7)$$

All the symbols are analogous to those used in the previous equations. Good agreement was obtained between the data calculated according to eqn. 7 and those obtained by Grushka *et al.*[3] for alkylbenzenes, as can be seen in Table III.

All the above equations are additive functions of log k', which is linearly dependent either on the carbon chain number, the reciprocal of the absolute temperature or log(methanol concentration), or their combination. These equations enable the chromatographer to calculate the capacity factor of any member of a homologous series at any mobile phase composition and/or at any temperature, and thus predict the retention behaviour of a solute or, conversely, to calculate the chromatographic conditions for a desired retention time.

Whereas eqns. 1, 4, 5 and 7 are restricted to members of homologous series, eqns. 2, 3 and 6 are general for any solute chromatographed at any mobile phase composition and/or at any temperature. The acquisition of the data for calculation is also very simple; for calculation according to eqns. 2 and 3 it is necessary to obtain only two values of the capacity factors of a compound at two different methanol concentrations c_1 and c_2, or at two different temperatures T_1 and T_2, respectively, which is a matter of making two injections. Only one injection of a mixture of two homologues is required for calculating k'_{n_3} according to eqn. 1.

Eqns. 4, 5 and 6, which contain two variables, require four values of measured capacity factors, and for calculating $k'_{n_3c_3T_3}$ (eqn. 7), where all the three parameters are varied, eight values of capacity factors have to be obtained. In all instances it is a matter of making up to four injections.

The error seldom exceeds the error of the chromatographic method itself (3%), and the higher errors occur especially in the following instances: (1) calculations of capacity factors of the first, non-linear members of a homologous series; and (2) calculations including the percentage of methanol in the mobile phase, which has been discussed above together with the derivation of eqn. 2. Even then the agreement between the measured and the calculated data is fairly good, as shown in Tables I–III.

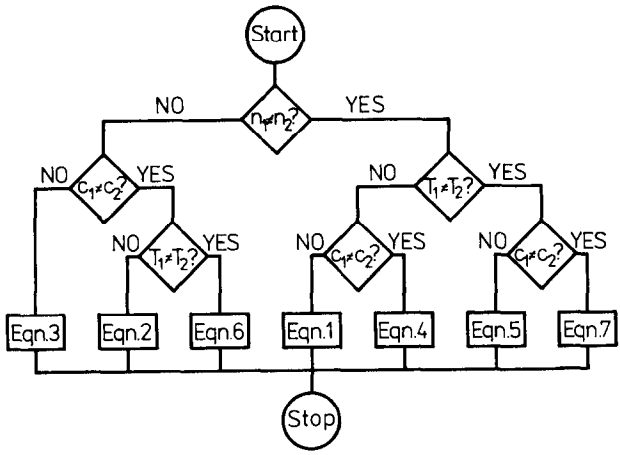

Fig. 2. Flow chart for calculating eqns. 1–7.

Eqn. 7 can be simplified to eqn. 4 provided that the capacity factors are not dependent on temperature, and hence capacity factors with subscripts T_1 are equal to those with subscripts T_2, *e.g.*, $k'_{n_1c_1T_1} = k'_{n_1c_1T_2}$ and $k'_{n_2c_2T_1} = k'_{n_2c_2T_2}$. Hence, the fourth term in eqn. 7 would be simplified to the third term in eqn. 4 and the third term in eqn. 7 would be cancelled out. In other words, it occurs in the case when $\lim_{T_2 \to T_1} (T_2 - T_1) = 0$.

Similarly, when the capacity factors are assumed to be independent of the methanol concentration, *e.g.*, $k'_{n_1c_1T_1} = k'_{n_1c_2T_1}$, eqn. 5 is obtained, and non-dependence on carbon number leads to eqn. 6. In an analogous way, eqn. 4 is reduced to either eqn. 1 or 2, eqn. 5 is simplified to either eqn. 1 or 3 and eqn. 6 to eqn. 2 or 3.

Unfortunaly, eqn. 7 itself cannot be used as a universal equation for calculating the capacity factors, even though it consists of all eqns. 1–6, but an appropriate equation must be chosen according to the problem to be solved. Nevertheless, the similarity of the equations aids in creating a programme for a calculator. For example, the entire eqn. 1 is a part of eqn. 4, which is a part of eqn. 7; eqn. 2 is a part of eqn. 6, etc. For the sake of clarity it is useful to supplement the missing subscripts with index 1, *e.g.*, $k'_{c_2} = k'_{n_1c_2T_1}$ and $k'_{n_3T_2} = k'_{n_3c_1T_2}$. The flow chart of the programme used for all the calculations in this paper is shown in Fig. 2.

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