Journal of Chromatography, 447 (1988) 177–181
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 566

Note

Characterization of mobile phases for the investigation of electrokinetic phenomena in liquid chromatography

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(Received April 11th, 1988)

The streaming current and the streaming potential incidental to it, which are applied in liquid chromatography for detection purposes, originate in special generating elements located after or in the chromatographic column[1]. The magnitude of the streaming current depends on, among other things, the dynamic viscosity (η) of the mobile phase, its relative permittivity (ε_r) and its conductivity (κ)[2]. Also, the dimensions of the generating elements, in which the maximum possible charge volume density in the streaming liquid is reached at the mobile phase flow-rate used, or the dimensions of earthed metal capillaries, in which the space charge carried by the liquid is completely discharged, depend on the values of ε_r and κ (ref. 3). Values of the parameters η, ε_r and κ have been tabulated for pure solvents only. In this work, these values have been measured for the binary mobile phases *n*-heptane–acetone, acetone–methanol, methanol–water and acetone–water of different compositions.

EXPERIMENTAL

Acetone and methanol of analytical-reagent grade (Lachema, Brno, Czechoslovakia) were purified and dried by rectification on a 40-plate glass bubble-cap column. Rectification, preservation of the rectified substances and all other operations with organic solvents and their mixtures were carried out in vessels dried with air cooled with solid carbon dioxide and protected against air humidity. *n*-Heptane (Laborchemie, Apolda, G.D.R.) was purified with alumina activated at 380°C. Distilled water was deionized with a mixture of cation-exchange resin (Ostion KS) and anion-exchange resin (Ostion AD) (Company for Chemical and Metallurgical Production, Ústí nad Labem, Czechoslovakia). Carbon dioxide was not removed from the water. The water content of the rectified solvents was established by Karl Fischer titration with coulometric indication. The total content of impurities in the solvents was established by measuring the conductivity (Table I).

0021-9673/88/$03.50

TABLE I

CONTENT OF WATER IN PURIFIED ORGANIC SOLVENTS AND RELATIVE PERMITTIVITIES (ε_r) AND CONDUCTIVITIES (κ) OF THE SOLVENTS PRIOR TO AND AFTER PURIFICATION

Solvent	*Water content (ppm)*	ε_r			κ ($S\ m^{-1}$)		
		Prior to purification	*After purification*	*Tabulated value*	*Prior to purification*	*After purification*	*Tabulated value****
Methanol	10	39.0	34.4	32.63*	$1.1 \cdot 10^{-4}$	$8.3 \cdot 10^{-5}$	$1.5 \cdot 10^{-7}$
Acetone	<400	23.0	20.8	20.7*	$1.9 \cdot 10^{-5}$	$9.2 \cdot 10^{-6}$	$4.9 \cdot 10^{-7}$
n-Heptane	–	1.9	1.9	1.924**	$1 \cdot 10^{-10}$	$<8 \cdot 10^{-11}$	$<10^{-14}$
Water	–	83.0	81.2	78.54*	$9.8 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	$5.89 \cdot 10^{-6}$

* At 25°C[4].
** At 20°C[5].
*** At 25°C[5].

Polyethylene vessels for the preparation of the samples and the connecting tubes and syringes for manipulation with the solvents and samples were washed with organic solvents and dried before use.

The conductivities (κ) of the samples and their relative permittivities (ε_r) were calculated from the capacity (C) and conductance (G) of a flow condenser with the volume of 4.7 ml and an air capacity of C_v = 6.63 pF derived from a capacity detection cell[6]. The non-thermostated condenser was connected to a Tesla BM 484 semi-automatic compensation bridge (Tesla, Brno, Czechoslovakia) enabling the quantities C and G simultaneously to be measured. The values of ε_r and κ were calculated from the relationships

$$\varepsilon_r = C/C_V \tag{1}$$

$$\kappa = \varepsilon_0 \varepsilon_r G/C \tag{2}$$

where ε_0 is the permittivity of a vacuum. The kinetic viscosity was measured with an Ubbelohde viscosimeter thermostated in a water bath at 20 ± 0.1°C. The densities of the solutions were determined pycnometrically.

RESULTS AND DISCUSSION

Titration indicated that the fractional distillation completely removed water from methanol. For the determination of water in rectified acetone, a titration agent completely inert to keto groups was not available. The actual water content of rectified acetone was, therefore, lower than that calculated from the consumption of titration agent given in Table I.

According to theory[6], the relative permittivity of a binary mixture of the solvents ($\varepsilon_{r_{1,2}}$) is a linear combination of the relative permittivities of the components (ε_{r_1}, ε_{r_2}):

$$\varepsilon_{r_{1,2}} = \varepsilon_{r_1} V_1 + \varepsilon_{r_2} V_2 \tag{3}$$

where V_1 and V_2 are volume fractions of solvents 1 and 2, respectively. The results confirm the validity of this relationship for all the combinations of the solvents over the whole range of concentrations (Fig. 1). From previous work[8], it is possible to assume that the relative permittivity of a binary mobile phases can be considered, with acceptible accuracy, to be a linear function of the composition even when the original solvents contain trace amounts of foreign matter.

The viscosity of the binary mobile phases was a linear combination of the viscosities of the components only for organic solvents (*n*-heptane–acetone and acetone–methanol) (Fig. 2). For mixtures of water with methanol, where the viscosity reaches a marked maximum, much better agreement with Van der Wal's data[9] than with the results published by Bates and Robinson[7] was found. The measured viscosities of the mixtures of water with acetone agreed with Van der Wal's data[9] only for acetone volume concentrations up to 40%.

The dependences of the conductivities on composition were non-linear at all four combinations of the solvents (Figs. 3 and 4). For acetone–methanol, acetone–

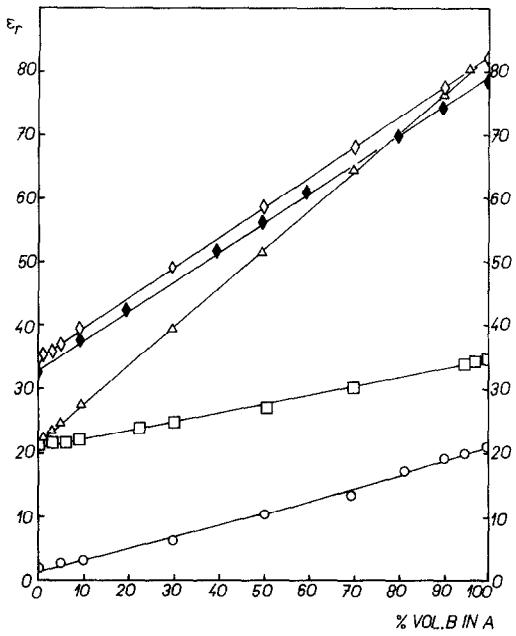

Fig. 1. Dependence of relative permittivity (ε_r) of binary mixtures of solvents on composition. ○, *n*-Heptane (A) and acetone (B); □, acetone (A) and methanol (B); △, acetone (A) and water (B); ◇, methanol (A) and water (B); ◆, methanol (A) and water (B) from ref. 7.

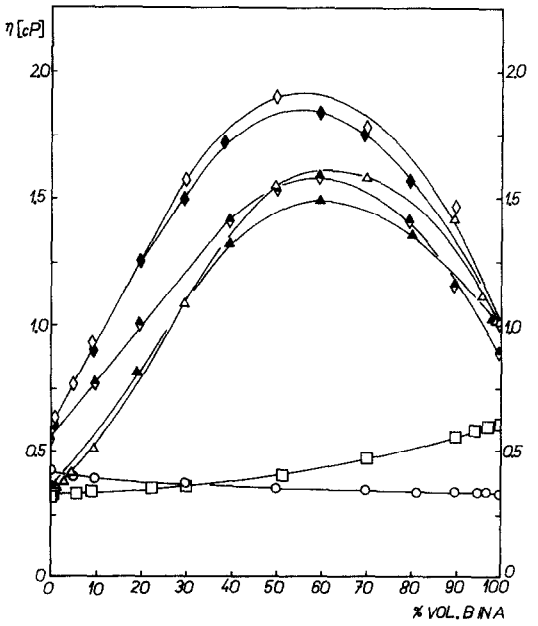

Fig. 2. Dependence of dynamic viscosity (η) of binary mixtures of solvents on composition. ◆, Methanol (A) and water (B)[9]; ◆, methanol (A) and water (B)[7]; ▲, acetone (A) and water (B)[9]. Other symbols as in Fig. 1.

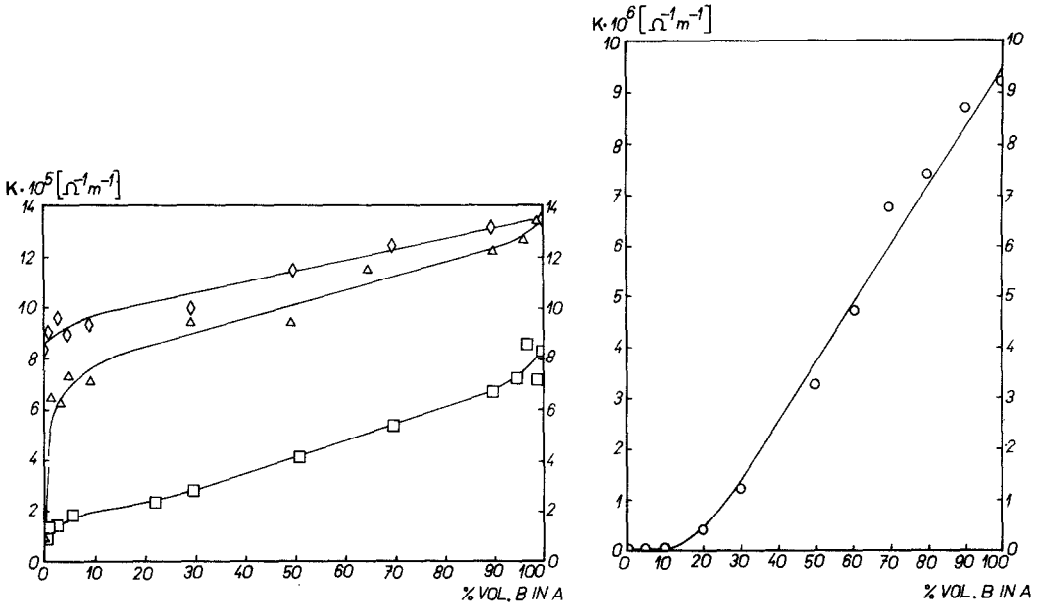

Fig. 3. Dependence of conductivity (κ) of binary mixtures of solvents on composition. Symbols as in Fig. 1.

Fig. 4. Dependence of the conductivity (κ) of a mixture of *n*-heptane (A) and acetone (B) on composition.

water and methanol–water, the conductivity varied with composition over an order of magnitude. For mixtures of water with methanol and acetone, the conductivity is a linear function of composition at volume fractions of water $\geqslant 0.2$. For acetone–methanol, the conductivity is a linear function of composition if the volume fraction of any of the components does not fall below 0.1. The conductivity of *n*-heptane–acetone varied over five orders of magnitude while a linear dependence of conductivity on composition was found for the volume fractions of acetone $\geqslant 0.3$.

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