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ORGANIC SALTS, LIQUID AT ROOM TEMPERATURE, AS MOBILE PHASES IN LIQUID CHROMATOGRAPHY

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SUMMARY

The synthesis of six alkylammonium salts of the general formula $R_{n-a} NH_a^+ X^-$, where R = ethyl, propyl, butyl or *sec.*-butyl, X^- = nitrate or thiocyanate, $n < 4$ and $a = 0, 1, 2$ or 3 is described. Four of these salts, which are liquid at room temperature, were previously unknown. Structural characterization was performed by NMR (1H , ^{13}C , ^{15}N), IR and fast-atom bombardment mass spectrometry. The above nitrate and thiocyanate salts and three other known liquid salts, triethylhexylammonium triethylhexylboride, tetraheptylammonium benzoate and tetraheptylammonium chloride, were characterized by standard physical measurement techniques to determine their suitability as chromatographic solvents. The physical properties measured include melting point, refractive index, UV spectra, miscibility with common organic solvents, aqueous solution pH, density and viscosity.

It was concluded that the alkylammonium nitrate and thiocyanate salts could be used as mobile phases in liquid chromatography when mixed with a second solvent of low viscosity. Suitable equations are given to predict the viscosity of mixtures of alkylammonium nitrate and thiocyanate salts in all volume proportions with water, methanol, acetonitrile, tetrahydrofuran and dichloromethane. The liquid organic salts form immiscible solvent pairs with non-polar organic solvents and should also be suitable for use in liquid-liquid chromatography and liquid-liquid extraction.

INTRODUCTION

Snyder has classified the common solvents used in liquid chromatography (LC) into eight groups, based on their ability to enter into orientation and proton donor-acceptor interactions¹. Solvents within the same selectivity group influence relative retention very little, while solvents from different groups may cause large changes in retention. Because of the limited efficiency of LC columns, these changes in selectivity become very important and represent the principal method for optimizing resolution. The introduction of new solvents with properties different from those characterized by Snyder would be a useful extension of the separating capability of LC. However, it would seem unlikely that new solvents of a selectivity radically different from that of solvents now used in LC will be found among covalently bond-

ed organic liquids. On the other hand, ionic liquids remain virtually unexplored as selective solvents in LC. The presence of coulombic forces opens up the possibility of exploiting the strong interactions possible with charge-bearing groups. Organic salts with their favorable ability to solubilize a wide variety of organic solutes, unusually large dipole moments, and strong Lewis acid–base interactions would seem to be good candidates for initial studies². However, to explore these possibilities it is first necessary to demonstrate that organic salts liquid at room temperature have solvent properties compatible with their use in LC. Information such as viscosity, compatibility with detection systems commonly used in LC, synthetic methods capable of preparing bulk quantities of organic salt solvents, and methods of characterizing impurities in synthesized batches of the liquid salts is generally unavailable.

Only a few, well-characterized organic salts are known to be liquid at room temperature². Principal among these are the haloaluminates, chlorocuprates and tetraalkylammonium tetraalkylborides. The haloaluminates and chlorocuprates are air sensitive, reactive and corrosive liquids, too inconvenient and too limited in application for use as general laboratory solvents. The tetraalkylammonium tetraalkylborides are air-stable liquids that have been used as solvents for spectroscopy, synthesis and electrochemistry^{3–10}. Their polarity is similar to that of common polar organic solvents. As both the anions and cations have a complete valence shell of electrons, Lewis acid–base interactions are absent, and the polarity of the salts is due to their ionic character, moderated by the large organic groups attached to the anions and cations. The difficult multi-step synthesis, lack of simple purification methods, and high viscosity of the tetraalkylammonium tetraalkylborides have limited their general use in analytical chemistry.

Several less well-characterized liquid organic salts are also known. The nitrite salts of ethylamine, dimethylamine and trimethylamine are liquids at room temperature but spontaneously decompose on standing¹¹. Ethylammonium nitrate is a stable liquid organic salt^{12,13}. This salt has been the subject of several recent studies stemming from assertions that it exhibits several of the characteristic properties uniquely associated with water. This water-like behavior was inferred from the heats, entropies and free energies of solution for non-polar gases in ethylammonium nitrate¹⁴, from a nearly ideal heat of mixing with water and from the ability of this solvent to produce micelles with surfactants^{15–17}. From measurements of heats of solution of alcohols in ethylammonium nitrate Mirejovsky and Arnett¹⁸ concluded that the most important characteristic of the salt is its high cohesive energy density and not the formation of a water-like hydrogen-bonded network. Tetrahexylammonium benzoate was used as a solvent for electrochemistry and kinetic studies¹⁹. Based on the solvent-mediated kinetics of the solvolysis of *tert.*-butyl chloride, the polarity of tetrahexylammonium benzoate was estimated to lie between those of ethanol and water. Di-*n*-butylammonium and di-*n*-propylammonium thiocyanates were reported to be liquids at room temperature that are stable to vacuum distillation²⁰. *n*-Butylamine hydrosulfide was reported to be a liquid that was rapidly decomposed on exposure to air²¹. Other liquid salts undoubtedly exist, but their syntheses are difficult to find in the literature. There are no comprehensive compilations of data for liquid organic salts. Some discussion of their solvent properties can be found in general reviews of organic molten salt chemistry^{2,22–27}.

In this paper, we wish to describe the synthesis and physical properties of four

new liquid organic salts and to compare their properties with previously described salts. The fundamental properties measured provide a basis for assessing their suitability for use as solvents in LC.

EXPERIMENTAL

The alkylamines were obtained from Aldrich (Milwaukee, WI, U.S.A.) and Fluka (Hauppauge, NY, U.S.A.). These were used as received, unless discolored, in which case they were distilled immediately before use. Tetrahexylammonium benzoate and tetraheptylammonium chloride were obtained from Eastman Kodak Co. (Rochester, NY, U.S.A.). Triethylhexylammonium triethylhexylboride was synthesized according to ref. 3. Nitric acid and ammonium thiocyanate were of analytical-reagent grade from J. T. Baker (Phillipsburg, NJ, U.S.A.). All solvents were of HPLC-grade from Burdick & Jackson (Muskegon, MI, U.S.A.).

The alkylammonium nitrate and thiocyanate salts were prepared by the following general methods. For the nitrate salts, 70% (v/v) nitric acid was added dropwise over about 2 h to a slight molar excess of an aqueous solution of the amine (70%, v/v). Throughout the addition, the reaction mixture was vigorously stirred and maintained at 0–25°C in an ice-salt bath. Upon completion of the reaction, water was evaporated in a rotary evaporator at 60°C, and impurities were removed by extraction with an immiscible organic solvent (Table I). Final traces of water and solvent were removed under high vacuum (< 0.2 Torr) until the salt attained constant viscosity.

For the thiocyanate salts, a slight excess of an aqueous solution of the alkylamine (70%, v/v) and an aqueous solution of ammonium thiocyanate (20–30%, w/v)

TABLE I
LIQUID ALKYLAMMONIUM SALTS

The following salts are solid at room temperature: nitrates: methylammonium, dimethylammonium, trimethylammonium, tetramethylammonium, diethylammonium, triethylammonium, tetraethylammonium, isopropylammonium, dipropylammonium, tripropylammonium, tetrapropylammonium, butylammonium, isobutylammonium, *sec.*-butylammonium, *tert.*-butylammonium, dibutylammonium and tetrabutylammonium; thiocyanates: methylammonium, dimethylammonium, trimethylammonium, tetramethylammonium, ethylammonium, diethylammonium, triethylammonium, tetraethylammonium, propylammonium, isopropylammonium, tripropylammonium, tetrapropylammonium, isobutylammonium, *tert.*-butylammonium, dibutylammonium, tributylammonium and tetrabutylammonium.

<i>Compound</i>	<i>Abbreviation</i>	<i>Solvent for extracting impurities</i>	<i>Color</i>
Ethylammonium nitrate	EAN	Dichloromethane	Colorless
Propylammonium nitrate	PAN	Toluene	Yellow
Tributylammonium nitrate	TBAN	Hexane	Orange
Dipropylammonium thiocyanate	DPAT	Toluene	Straw yellow
Butylammonium thiocyanate	BAT	Toluene	Straw yellow
<i>sec.</i> -Butylammonium thiocyanate	sBAT	Toluene	Straw yellow
Triethylhexylammonium triethylhexylboride	TEHAB		Yellow
Tetrahexylammonium benzoate	QHAB		Yellow
Tetraheptylammonium chloride	QHAC		Yellow

were stirred vigorously under gentle reflux (70–80°C). The reaction was continued until the evolution of ammonia ceased; depending on the amine this required from 4 h to 2 days. Water was removed in the rotary evaporator and the liquid salt was purified by extraction with an immiscible organic solvent (Table I). Final traces of water and solvent were removed under vacuum (<0.2 Torr) until the salt reached constant viscosity. The yield of the nitrate and thiocyanate salts were 90–100% of the theoretical value.

Viscosity measurements were made with a Cannon–Fenske capillary viscometer (Schott-Geräte, Yonkers, NY, U.S.A.), calibrated with water and glycerol. Densities were measured with a Gay–Lussac type pycnometer (Ace Glass, Vineland, NJ, U.S.A.), calibrated with water. Refractive index (RI) values were measured with an Abbé refractometer (Bausch & Lomb, Rochester, NY, U.S.A.). The molar refraction was calculated from eqn. 1²⁸:

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot V_m \quad (1)$$

where R = molar refraction, n = refractive index measured at the d line for sodium and V_m = molar volume.

A Sensorex combination pH electrode (Irvine, CA, U.S.A.) and a Corning Model 110 digital pH meter (Corning, NY, U.S.A.) were used for aqueous solution pH measurements. Melting points were measured with an alcohol thermometer, after first freezing the salt and allowing it to melt slowly by immersion into a series of slush baths of successively higher temperatures. The decomposition temperature was measured by sealing a sample of the salt in a melting point capillary and slowly heating it to above room temperature in an oil bath. The temperature at which a color change occurred was taken to be the decomposition temperature. UV spectra of the salts were recorded without solvent in 0.1-mm quartz cells on a Varian Model 118 spectrophotometer (Palo Alto, CA, U.S.A.). IR spectra were recorded as thin films between sodium chloride plates, using a Nicolet 20DX FTIR Spectrometer (Madison, WI, U.S.A.). ¹H (300 MHz), ¹³C (75.5 MHz) and ¹⁵N (30.4 MHz) NMR spectra were recorded for the neat liquid salts with external calibration ([²H]chloroform or formamide) on a General Electric QE-300 or GN-300 spectrometer (Freemont, CA, U.S.A.). Fast-atom bombardment (FAB) mass spectra were recorded with a Kratos MS 80-RAF mass spectrometer (Westwood, NJ, U.S.A.). The FAB source was operated at 5.8 kV, tube current 30 μA, with argon as the primary particle. Positive-ion mass spectra were recorded at an accelerating potential of 4 kV, scan rate 30 s, mass range 50–1000 a.m.u., and resolution of 1500.

RESULTS AND DISCUSSION

The primary aim of this research was to synthesize new liquid organic salts suitable for use as chromatographic solvents. As there is no known relationship between the melting point of an organic salt and its chemical constituent groups, some empirical conclusions had to be drawn. The availability of starting materials, ease of preparation and previous reports of low melting points were taken into consideration. This led to the selection of the alkylammonium nitrate and thiocyanate salts for

study. These observations proved to be sound, as four new liquid salts were discovered among all possible alkylammonium nitrate and thiocyanate salts containing either methyl, ethyl, propyl or butyl groups. The new liquid salts are indicated in Table I, together with previously discovered liquid salts evaluated in this study. Salts that were found to be solid at room temperature are summarized in the footnote to Table I. All methyl salts and all tetraalkylammonium nitrate and thiocyanate salts were found to be solids. Otherwise, it is impossible to indicate properties of the cation that are important for the formation of low-melting salts. Dibutylammonium thiocyanate, previously reported to be a liquid²⁰, was prepared as a solid in this study.

The series of alkylammonium nitrate and thiocyanate salts prepared by us considerably expands the total number of known liquid organic salts. Furthermore, these salts are easy to prepare in high yield and purity. If the indicated experimental conditions are followed, by-product formation is not observed, and the only purification step required is solvent extraction. Discolored batches of salt, prepared in preliminary studies, could frequently be purified by treatment of a solution of the salt with decolorizing charcoal. The liquid alkylammonium nitrate and thiocyanate salts are air-stable. Most salts are mildly hygroscopic, and prolonged contact with the atmosphere should be avoided during general laboratory manipulations.

The composition and presence of contaminants in the liquid organic salts is easily determined by spectroscopic means. Relevant data are summarized in Tables II and III. The IR spectra show characteristic absorption at 1645–1620, 1350–1250, 870–850 and 760–750 cm^{-1} for the nitrate anion. Bands at 2065–2055 and 770–740 cm^{-1} are characteristic of the thiocyanate anion. The ammonium ion shows broad N–H stretching bands in the region 3300–3000 cm^{-1} . The UV absorption spectra of the nitrate salts (Fig. 1) show a moderately intense band or shoulder between 260 and 300 nm. The long-wavelength absorption of the thiocyanate anion, centered at 275 nm, is much weaker and changes little with variation of the alkylammonium cation. The ¹⁵N NMR spectra show characteristic chemical shifts for the alkylammonium cation (30–55 ppm), nitrate anion (360–380 ppm) and thiocyanate anion (202–207 ppm).

The alkylammonium salts do not yield normal electron-impact or chemical-ionization mass spectra. In the last few years, FAB has become recognized as the preferred method of ionization for ionic molecules such as alkylammonium salts^{29,30}. The FAB mass spectra of the alkylammonium nitrate and thiocyanate salts are characterized by the formation of cluster ions of the type $[(AB)_nAH_x]^+$, where A = cation, B = anion, n = integer from 0 to 6, and x = integer from 0 to 2 (Table III). Representative mass spectra are shown in Fig. 2 for ethylammonium nitrate and in Fig. 3 for butylammonium thiocyanate. No support matrix, such as glycerol, is required to record mass spectra for the liquid organic salts.

Physical properties of the room temperature liquid organic salts are summarized in Table IV. The viscosity of the alkylammonium nitrate and thiocyanate salts varies from about 25 to 125 cP. These values are considerably lower than those found for the other liquid salts summarized in Table IV. Increasing temperature causes an exponential decline in the viscosity of the alkylammonium nitrate and thiocyanate salts, at least for the temperature range investigated (Fig. 4). The data can be fitted to the relationship given in eqn. 2 by using the coefficients summarized in Table V.

$$\ln \eta = A_1 + A_2 \cdot t \quad (2)$$

TABLE II
SPECTROSCOPIC PROPERTIES OF LIQUID ORGANIC SALTS

Compound	UV (nm) λ_{max}	IR (cm^{-1})		NMR (ppm)*		J_{NH} (Hz)	δ_C (C)	Cation	Anion
		$\nu(NO_3)$	$\nu(SCN)$	$\delta_H(NH)$	$\delta_N(N)$				
EAN	292	1625		7.6	32.2(q)	75.5	12.4	36.3	
PAN	294	1631		8.0	30.6(q)	74.7	10.8	21.1	42.4
TBAN	268	1630		3.7	53.4	375.5	13.7	20.3	53.0
DPAT	275		2065	8.0	48.1	203.8	11.6	20.1	50.1
BAT	275		2060	8.1	38.1	205.9	13.9	20.1	29.6
sBAT	273		2054	7.5	50.5	206.9	10.3	18.1	27.9

* q = quartet.

TABLE III
FAST-ATOM BOMBARDMENT MASS SPECTRA OF LIQUID ORGANIC SALTS

Organic salt	Base peak	Most abundant ions
EAN	(AB)A	(AB) ₅ A, (2.2) → (AB) ₄ A, (3.9) → (AB) ₃ A, (13) → (AB) ₂ A, (34.7) → (AB)A, (100)
PAN	(C ₃ H ₇) ₂ N ⁺	(AB) ₄ AH, (3) → (AB) ₃ AH, (6) → (AB) ₂ A, (18) → (AB)A, (45)
TBAN	AH	(AB)AH ₂ , (29) → AH, (100)
DPAT	A	(AB) ₃ AH, (1.0) → (AB) ₂ AH, (7) → (AB)A, (57) → A, (100); (A ₂ -H), (2.9); [C ₃ H ₇ NH=CH ₂] ⁺ , (90)
BAT	A	(AB) ₂ AH ₂ , (0.2) → (AB) ₄ AH, (0.2) → (AB) ₃ AH, (1.5) → (AB) ₂ AH, (3) → (AB)A, (4.4) → A, (100); (A ₂ -H), (12.6)
sBAT	A	(AB) ₃ A, (0.1) → (AB) ₂ A, (0.2) → (AB)A, (1.1) → A, (100); A ₂ -H, (3.9); [A + 40] ⁺ , (9.5)
TEHAB	A	[A + C ₂ H ₄] ⁺ , (2.7); [C ₆ H ₁₃ N(C ₂ H ₅) ⁺ , (12.5); [(C ₂ H ₅) ₃ NH] ⁺ , (4.6); [(C ₂ H ₅) ₂ N=CH ₂] ⁺ , (17.7)

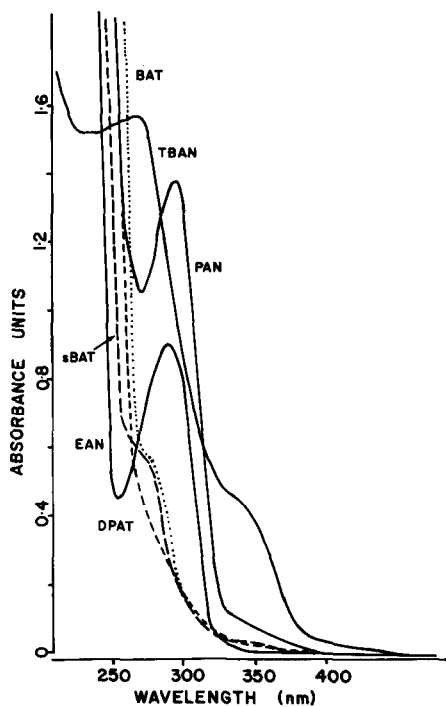


Fig. 1. UV spectra of liquid alkylammonium nitrate and thiocyanate salts.

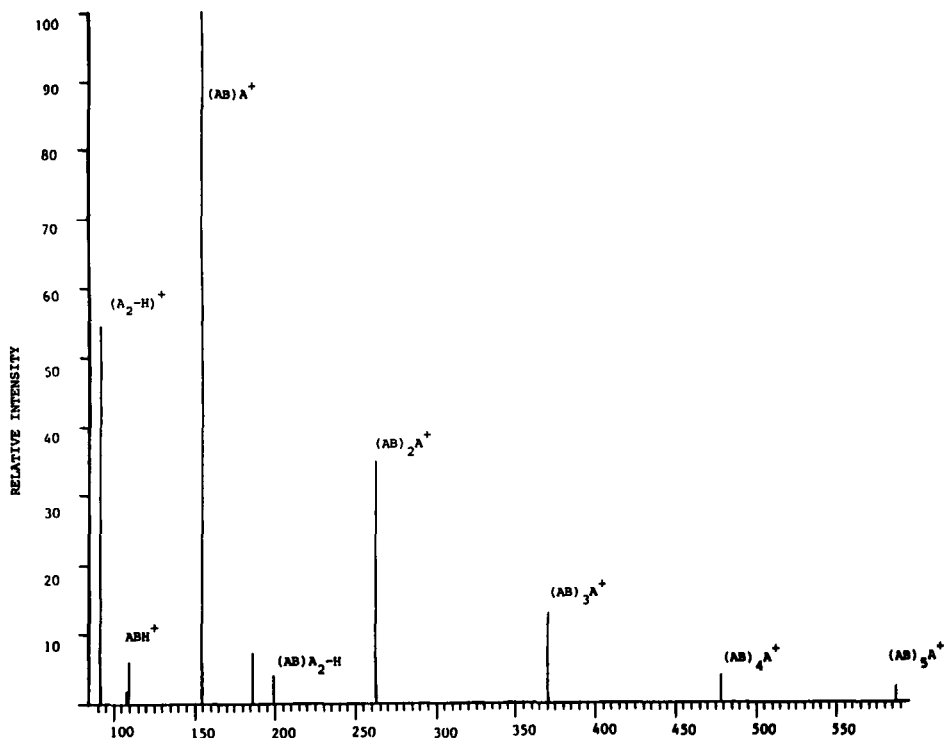


Fig. 2. FAB mass spectrum of ethylammonium nitrate.

TABLE IV
PHYSICAL PROPERTIES OF LIQUID ORGANIC SALTS

Compound	Melting point (°C)	Viscosity (cP)	Density (g/ml)	Molar volume	Refractive index	Molar refraction	Decomposition temperature (°C)
EAN	12.5	26.91	1.2191	88.59	1.4520	23.90	170
PAN	4.0	63.70	1.1568	105.46	1.4550	28.61	120
TBAN	21.5	89.43	0.9963	249.92	1.4592	68.35	119
DPAT	5.5	37.80	0.9663	165.58	1.5018	48.85	140
BAT	20.5	84.06	1.0115	130.50	1.5170	39.48	130
sBAT	22	122.60	1.0132	130.28	1.5262	40.00	> 200
TEHAB	< -75	257.67	0.8471	434.42	1.4805	123.52	87
QHAB	-50	894.58	0.9383	491.31	1.4900	142.05	
QHAC	-9	597.81*	0.8817*				

* Measured at 35°C; all other values measured at 25 ± 0.1°C.

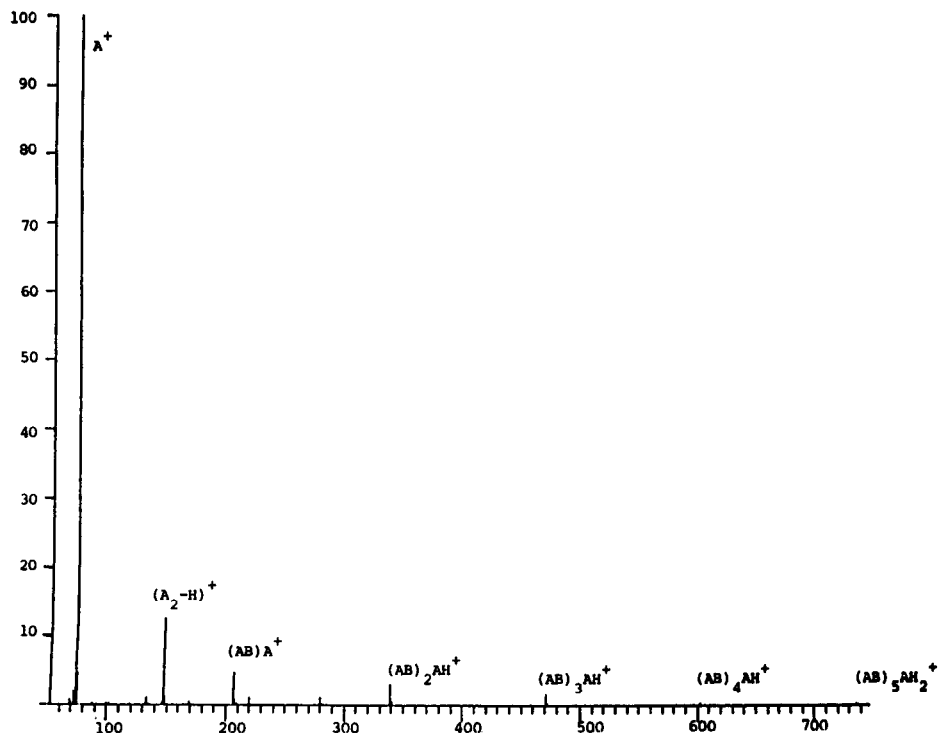


Fig. 3. FAB mass spectrum of butylammonium thiocyanate.

where η = viscosity of the liquid salt at temperature t and t = temperature in °C.

Operation of a liquid chromatograph at temperatures above those studied would be inconvenient and we will show later that dilution of the liquid salt with an organic solvent of low viscosity is a more practical means of controlling viscosity for chromatographic applications.

Two general trends in the values for the RI of the liquid organic salts can be discerned. The RI of the thiocyanate salts are larger than those of the nitrate salts (Table IV). The molar refraction of the liquid organic salts is a simple function of the number of carbon atoms in the alkyl groups attached to the ammonium cation and is largely insensitive to the type of carbon atom (primary, secondary, etc.) in the chain (Fig. 5). For confirmation, some entries for solid salts obtained as liquids prior to solidification have been added to Fig. 5.

For use in LC the viscosity of the liquid organic salts will have to be reduced to values close to those of conventional organic solvents. The only way to achieve this is by using elevated temperatures or by dilution with a miscible solvent of low viscosity. The miscibility of the liquid organic salts in solvents frequently used in LC is summarized in Table VI. All the nitrate and thiocyanate salts are insoluble in hexane. Their solubility increases with the polarity of the organic solvent, and most salts are miscible with a wide range of common solvents including water. However, increasing the size of the alkyl portion of the cation decreases the solubility of the nitrate and thiocyanate salts in water.

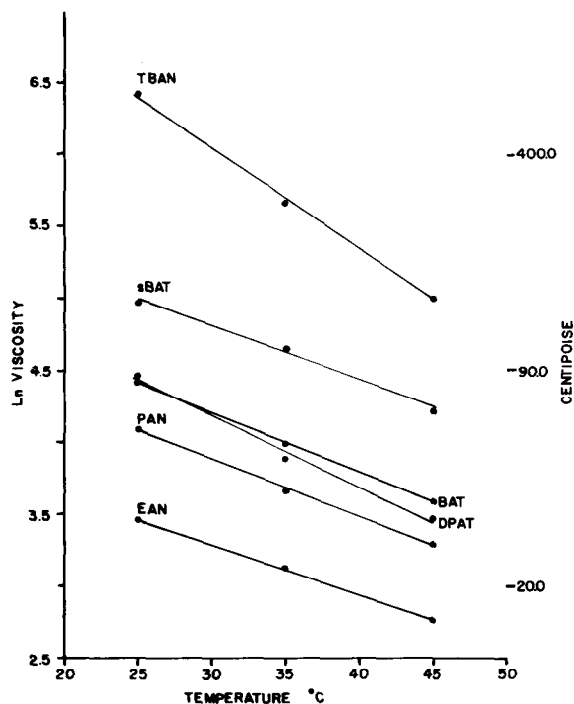


Fig. 4. Change in viscosity as a function of temperature for the pure alkylammonium nitrate and thiocyanate salts.

The density of binary mixtures of liquid alkylammonium nitrate and thiocyanate salts in water, methanol, acetonitrile, tetrahydrofuran and dichloromethane can be represented by a simple linear equation (eqn. 3)

$$\rho_{\text{SOL}} = A_1 + A_2\theta \quad (3)$$

where ρ_{SOL} = density of the binary solvent mixture, A_1 = intercept $\approx \rho_0$, ρ_0 =

TABLE V

COEFFICIENTS FOR THE CHANGE IN VISCOSITY OF THE ALKYLAMMONIUM NITRATE AND THIOCYANATE SALTS AS A FUNCTION OF TEMPERATURE (25–45°C)

Liquid salt	A_1	A_2 ($\times 10^2$)	Correlation coefficient
EAN	4.33	-3.49	1.00
PAN	5.09	-4.01	1.00
TBAN	8.18	-7.12	0.99
DPAT	5.69	-5.01	1.00
BAT	5.49	-4.25	1.00
sBAT	5.94	-3.78	0.99

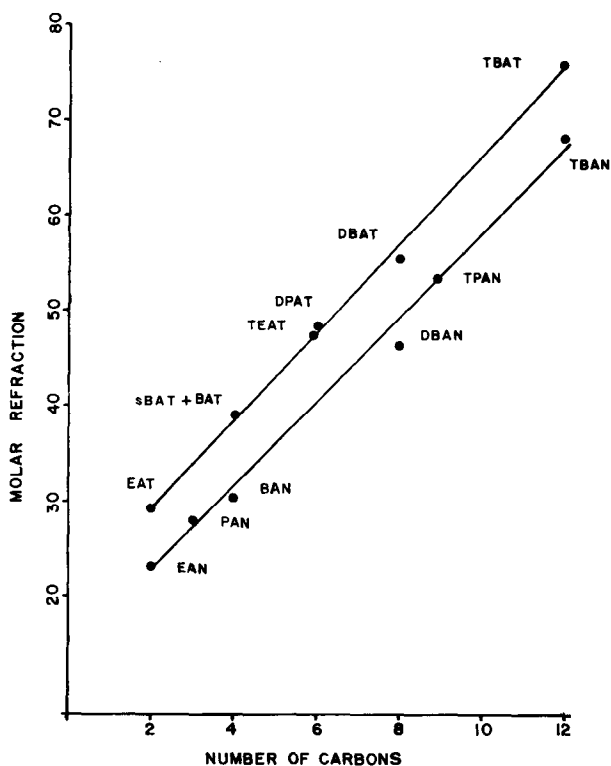


Fig. 5. Relationship between the molar refraction of the liquid organic salts and the number of carbon atoms in the alkylammonium cation. The following salts were measured in the liquid state prior to solidifying: EAT = ethylammonium thiocyanate, DBAT = dibutylammonium thiocyanate, TBAT = tributylammonium thiocyanate, BAN = butylammonium nitrate, DBAN = dibutylammonium nitrate, and TPAN = tripropylammonium nitrate.

TABLE VI

MISCIBILITY OF LIQUID ORGANIC SALTS WITH COMMON SOLVENTS

M = Miscible, I = immiscible, % = solubility of salt in solvent on a v/v basis.

Salt	Water	Methanol	Acetonitrile	Tetrahydrofuran	Dichloromethane	Hexane
EAN	M	M	M	M	I	I
PAN	M	M	M	M	60%	I
TBAN	40%	M	M	M	M	I
DPAT	M	M	M	M	M	I
BAT	M	M	M	M	M	I
sBAT	M	M	M	M	*	I
TEHAB	I	M	M	M	M	M
QHAB	M	M	M	M	M	30%
QHAC	M	M	M	M	M	30%

* Forms a single-layer cloudy dispersion.

TABLE VII

VARIATION OF DENSITY WITH VOLUME PERCENT OF LIQUID ORGANIC SALTS AND TEMPERATURE

Organic salt	Solvent	Temperature (°C)	Intercept (A_1)	Relative error (%) in assuming $A_1 = \rho_0^*$	Slope (A_2)	Correlation coefficient
EAN	Water	25	0.946	-5.1	$1.91 \cdot 10^{-3}$	1.00
		35	0.942		$1.88 \cdot 10^{-3}$	1.00
		45	0.939		$1.87 \cdot 10^{-3}$	1.00
	Methanol	25	0.751	-4.5	$3.87 \cdot 10^{-3}$	1.00
		35	0.746		$3.85 \cdot 10^{-3}$	1.00
		45	0.733		$3.89 \cdot 10^{-3}$	1.00
	Acetonitrile	25	0.735	-5.3	$4.00 \cdot 10^{-3}$	1.00
		35	0.732		$3.99 \cdot 10^{-3}$	1.00
		45	0.722		$4.03 \cdot 10^{-3}$	1.00
PAN	Water	25	0.946	-5.1	$1.36 \cdot 10^{-3}$	0.99
		35	0.942		$1.35 \cdot 10^{-3}$	1.00
		45	0.939		$1.33 \cdot 10^{-3}$	1.00
	Methanol	25	0.745	-5.3	$3.34 \cdot 10^{-3}$	1.00
		35	0.742		$3.34 \cdot 10^{-3}$	1.00
		45	0.734		$3.36 \cdot 10^{-3}$	1.00
	Acetonitrile	25	0.744	-4.2	$3.31 \cdot 10^{-3}$	1.00
		35	0.733		$3.41 \cdot 10^{-3}$	1.00
		45	0.724		$3.46 \cdot 10^{-3}$	1.00
	Tetrahydrofuran	25	0.875	-1.0	$1.97 \cdot 10^{-3}$	0.98
		35	0.866		$2.04 \cdot 10^{-3}$	0.98
		45	0.859		$2.07 \cdot 10^{-3}$	0.98
TBAN	Methanol	25	0.738	-6.2	$1.80 \cdot 10^{-3}$	0.98
		35	0.734		$1.81 \cdot 10^{-3}$	1.00
		45	0.725		$1.83 \cdot 10^{-3}$	1.00
	Acetonitrile	25	0.731	-5.9	$1.88 \cdot 10^{-3}$	1.00
		35	0.725		$1.90 \cdot 10^{-3}$	1.00
		45	0.711		$1.97 \cdot 10^{-3}$	1.00
	Tetrahydrofuran	25	0.836	-5.1	$8.25 \cdot 10^{-4}$	1.00
		35	0.831		$8.31 \cdot 10^{-4}$	1.00
		45	0.821		$8.80 \cdot 10^{-4}$	1.00
DPAT	Dichloromethane	25	1.241	-5.8	$-3.18 \cdot 10^{-3}$	1.00
	Water	25	0.993	-0.4	$-3.34 \cdot 10^{-4}$	0.97
		35	0.993		$-3.35 \cdot 10^{-4}$	0.97
		45	0.989		$-3.47 \cdot 10^{-4}$	0.97
	Methanol	25	0.797	1.3	$1.71 \cdot 10^{-3}$	0.99
		35	0.789		$1.71 \cdot 10^{-3}$	1.00
		45	0.752		$2.06 \cdot 10^{-3}$	0.99
	Acetonitrile	25	0.775	-0.3	$1.89 \cdot 10^{-3}$	1.00
		35	0.765		$1.94 \cdot 10^{-3}$	1.00
		45	0.757		$1.96 \cdot 10^{-3}$	1.00
	Tetrahydrofuran	25	0.888	0.8	$8.03 \cdot 10^{-4}$	0.96
		35	0.874		$8.64 \cdot 10^{-4}$	0.99
		45	0.859		$9.49 \cdot 10^{-4}$	1.00
	Dichloromethane	25	1.317	0.0	$-3.50 \cdot 10^{-3}$	1.00
		35	1.299		$-3.39 \cdot 10^{-3}$	1.00

TABLE VII (continued)

Organic salt	Solvent	Temperature (°C)	Intercept (A_1)	Relative error (%) in assuming $A_1 = \rho_o^*$	Slope (A_2)	Correlation coefficient
BAT	Water	25	0.940	-10.5	$9.86 \cdot 10^{-5}$	0.78
		35	0.937		$8.84 \cdot 10^{-5}$	0.90
		45	0.933		$5.23 \cdot 10^{-5}$	0.83
	Methanol	35	0.937	-5.2	$8.84 \cdot 10^{-5}$	0.90
		45	0.933		$5.23 \cdot 10^{-5}$	0.83
		25	0.746		$2.06 \cdot 10^{-3}$	1.00
	Acetonitrile	35	0.742	-5.9	$2.05 \cdot 10^{-3}$	1.00
		45	0.739		$1.99 \cdot 10^{-3}$	1.00
		25	0.731		$2.20 \cdot 10^{-3}$	1.00
	Tetrahydrofuran	35	0.730	-4.3	$2.16 \cdot 10^{-3}$	1.00
		45	0.719		$2.20 \cdot 10^{-3}$	1.00
		25	0.843		$1.09 \cdot 10^{-3}$	0.99
	Dichloromethane	35	0.839	-6.0	$1.09 \cdot 10^{-3}$	0.99
		45	0.832		$1.11 \cdot 10^{-3}$	0.98
		25	1.238		$-2.84 \cdot 10^{-3}$	1.00
sBAT	Water	25	0.993	-0.4	$1.87 \cdot 10^{-4}$	0.91
		35	0.990		$1.57 \cdot 10^{-4}$	0.89
		45	0.987		$1.29 \cdot 10^{-4}$	0.86
	Methanol	25	0.805	2.4	$2.10 \cdot 10^{-3}$	1.00
		35	0.794		$2.14 \cdot 10^{-3}$	1.00
		45	0.768		$2.34 \cdot 10^{-3}$	1.00
	Acetonitrile	25	0.776	-0.1	$2.37 \cdot 10^{-3}$	1.00
		35	0.704		$2.88 \cdot 10^{-3}$	0.98
		45	0.702		$2.85 \cdot 10^{-3}$	0.97
	Tetrahydrofuran	25	0.907	3.0	$1.09 \cdot 10^{-3}$	0.99
		35	0.876		$1.32 \cdot 10^{-3}$	1.00
		45	0.868		$1.33 \cdot 10^{-3}$	1.00
	Dichloromethane	25	1.217	-7.5	$-2.17 \cdot 10^{-3}$	0.96
		35	1.204		$-2.07 \cdot 10^{-3}$	0.98

* Relative error $(A_1 - \rho_o)/\rho_o$ (%), where ρ_o = density of the organic solvent at 25°C.

density of the organic solvent, A_2 = slope and Θ = volume percent of organic liquid salt.

The coefficients A_1 and A_2 for different solvent mixtures at 25, 35 and 45°C are summarized in Table VII. The agreement of the experimental data with eqn. 3 is very good, except for BAT and sBAT in water. Also, the coefficient A_1 , obtained by curve fitting, is approximately equal to the density of the diluting solvent at 25°C. The average error in assuming $A_1 = \rho_o$ is about 5% (see Table VII). The influence of dilution with an organic solvent and temperature on the viscosity of the alkylammonium nitrate and thiocyanate salts is summarized in Tables VIII and IX. In solvents of low dielectric constant, tetrahydrofuran and dichloromethane, the viscosity of the liquid organic salt solutions declines exponentially with increasing volume percent of the organic solvent, according to Eqn. 4 (except for TBAN in tetrahydrofuran). This applies to the other salts investigated as well as to the nitrate and thiocyanate salts (Fig. 6).

$$\ln \eta_{\text{sol}} = A_1 + A_2\Theta \quad (4)$$

TABLE VIII

LINEAR VARIATION OF VISCOSITY WITH PERCENT VOLUME OF LIQUID ORGANIC SALT AND TEMPERATURE

Organic salt	Solvent	Temperature (°C)	A_1	A_2	Correlation coefficient
EAN	Acetonitrile	25	-1.163	$4.587 \cdot 10^{-2}$	1.00
		35	-1.269	$4.346 \cdot 10^{-2}$	1.00
		45	-1.317	$4.047 \cdot 10^{-2}$	1.00
PAN	Tetrahydrofuran	25	-0.473	$4.600 \cdot 10^{-2}$	1.00
		35	-0.587	$4.295 \cdot 10^{-2}$	1.00
		45	-0.697	$3.968 \cdot 10^{-2}$	1.00
DPAT	Tetrahydrofuran	25	-1.055	$5.493 \cdot 10^{-2}$	1.00
		35	-1.314	$5.075 \cdot 10^{-2}$	0.99
		45	-1.371	$4.673 \cdot 10^{-2}$	0.98
	Dichloromethane	25	-1.340	$5.627 \cdot 10^{-2}$	0.98
		35	-1.359	$5.092 \cdot 10^{-2}$	0.99
BAT	Tetrahydrofuran	25	-0.638	$5.062 \cdot 10^{-2}$	0.99
		35	-0.945	$4.924 \cdot 10^{-2}$	1.00
		45	-0.889	$4.527 \cdot 10^{-2}$	1.00
sBAT	Dichloromethane	25	-1.060	$5.482 \cdot 10^{-2}$	1.00
		35	-1.375	$5.872 \cdot 10^{-2}$	0.99
	Tetrahydrofuran	25	-0.715	$5.716 \cdot 10^{-2}$	1.00
		35	-1.209	$5.354 \cdot 10^{-2}$	1.00
		45	-1.238	$6.066 \cdot 10^{-2}$	0.99
	Dichloromethane	35	-1.376	$5.826 \cdot 10^{-2}$	0.99

where η_{SOL} = viscosity of the liquid salt and organic solvent mixture, A_1 = intercept $\approx \ln \eta_0$, A_2 = slope, η_0 = viscosity of the organic solvent at 25°C and Θ = volume percent of organic liquid salt. For the alkylammonium nitrate and thiocyanate salts in water, methanol and acetonitrile, that is solvents of higher dielectric constant, the change in viscosity upon dilution is given by a third order polynomial, eqn. 5 (except for EAN in acetonitrile)

$$\ln \eta_{\text{SOL}} = A_1 + A_2\Theta + A_3\Theta^2 + A_4\Theta^3 \quad (5)$$

where η_{SOL} = viscosity of the liquid salt and organic solvent mixture, A_1, A_2, A_3, A_4 = coefficients obtained by curve fitting (Table IX), $A_1 \approx \ln \eta_0$, η_0 = viscosity of the organic solvent at 25°C and Θ = volume percent of liquid organic salt. The coefficients for eqn. 5 are summarized in Table IX, together with the chi-squared values, obtained by curve fitting. Apart from the values for BAT and sBAT in water the agreement is very good. If the values for the coefficient A_1 in Tables VIII and IX are averaged (\bar{A}_1), a reasonable agreement between \bar{A}_1 and the viscosity of the pure organic solvent at 25°C is obtained; \bar{A}_1 (methanol) = $\ln 0.53$ ($\eta_0 = 0.54$), \bar{A}_1 (acetonitrile) = $\ln 0.34$ ($\eta_0 = 0.34$), \bar{A}_1 (water) = $\ln 0.83$ (excluding BAT and sBAT) ($\eta_0 = 0.89$), \bar{A}_1 (tetrahydrofuran) = $\ln 0.50$ ($\eta_0 = 0.46$) and \bar{A}_1 (dichloromethane) = $\ln 0.30$ ($\eta_0 = 0.41$). Some representative examples of the influence of solvent dilution on the viscosity of DPAT solutions are shown in Fig. 7. Dilution with an organic solvent of low viscosity is an effective means of bringing the viscosity of the

TABLE IX

VARIATION OF VISCOSITY WITH PERCENT VOLUME OF LIQUID ORGANIC SALT AND TEMPERATURE

<i>Organic salt</i>	<i>Solvent</i>	<i>Temperature (°C)</i>	A_1	A_2	A_3	A_4	Chi^2
EAN	Water	25	-0.243	0.018	$-1.3 \cdot 10^{-4}$	$3.2 \cdot 10^{-6}$	$-1.8 \cdot 10^{-6}$
		35	-0.516	0.022	$-2.2 \cdot 10^{-4}$	$3.7 \cdot 10^{-6}$	$-4.9 \cdot 10^{-6}$
		45	-0.658	0.023	$-3.4 \cdot 10^{-4}$	$4.5 \cdot 10^{-6}$	$-1.3 \cdot 10^{-5}$
	Methanol	25	-0.584	0.030	$-3.9 \cdot 10^{-5}$	$1.4 \cdot 10^{-6}$	$-4.3 \cdot 10^{-6}$
		35	-0.742	0.030	$-8.3 \cdot 10^{-5}$	$1.7 \cdot 10^{-6}$	$-5.8 \cdot 10^{-6}$
		45	-0.959	0.036	$-2.5 \cdot 10^{-4}$	$2.6 \cdot 10^{-6}$	$-1.1 \cdot 10^{-5}$
PAN	Water	25	-0.163	0.022	$-2.6 \cdot 10^{-4}$	$4.7 \cdot 10^{-6}$	$-2.3 \cdot 10^{-5}$
		35	-0.395	0.022	$-3.3 \cdot 10^{-4}$	$5.2 \cdot 10^{-6}$	$-1.4 \cdot 10^{-5}$
		45	-0.366	0.0055	$1.2 \cdot 10^{-4}$	$1.9 \cdot 10^{-6}$	$9.0 \cdot 10^{-8}$
	Methanol	25	-0.708	0.043	$-4.1 \cdot 10^{-4}$	$4.6 \cdot 10^{-6}$	$1.4 \cdot 10^{-5}$
		35	-0.763	0.033	$-2.0 \cdot 10^{-4}$	$3.1 \cdot 10^{-6}$	$1.9 \cdot 10^{-5}$
		45	-0.880	0.030	$-1.3 \cdot 10^{-4}$	$2.5 \cdot 10^{-6}$	$-1.5 \cdot 10^{-5}$
	Acetonitrile	25	-0.938	0.035	$4.5 \cdot 10^{-5}$	$1.1 \cdot 10^{-6}$	$4.1 \cdot 10^{-6}$
		35	-1.044	0.031	$7.9 \cdot 10^{-5}$	$8.3 \cdot 10^{-7}$	$-2.1 \cdot 10^{-6}$
		45	-1.153	0.032	$5.0 \cdot 10^{-5}$	$7.8 \cdot 10^{-7}$	$-1.7 \cdot 10^{-6}$
TBAN	Methanol	25	-0.744	0.039	$-7.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-5}$	$1.0 \cdot 10^{-4}$
		35	-0.804	0.031	$-4.8 \cdot 10^{-4}$	$8.1 \cdot 10^{-6}$	$-3.1 \cdot 10^{-5}$
		45	-0.963	0.031	$-4.8 \cdot 10^{-4}$	$7.3 \cdot 10^{-6}$	$-2.3 \cdot 10^{-7}$
	Acetonitrile	25	-1.146	0.033	$-5.1 \cdot 10^{-4}$	$9.3 \cdot 10^{-6}$	$4.9 \cdot 10^{-6}$
		35	-1.182	0.025	$-3.0 \cdot 10^{-4}$	$7.3 \cdot 10^{-6}$	$-3.5 \cdot 10^{-5}$
		45	-1.303	0.027	$-3.8 \cdot 10^{-4}$	$7.3 \cdot 10^{-6}$	$-2.6 \cdot 10^{-5}$
	Tetrahydrofuran	25	-0.697	0.028	$5.3 \cdot 10^{-5}$	$3.8 \cdot 10^{-6}$	$-2.9 \cdot 10^{-5}$
		35	-0.840	0.028	$7.9 \cdot 10^{-5}$	$3.0 \cdot 10^{-6}$	$-2.8 \cdot 10^{-5}$
		45	-1.004	0.036	$-1.8 \cdot 10^{-4}$	$4.4 \cdot 10^{-6}$	$-2.9 \cdot 10^{-5}$
DPAT	Water	25	-0.157	0.028	$-1.7 \cdot 10^{-4}$	$3.6 \cdot 10^{-6}$	$-2.0 \cdot 10^{-5}$
		35	-0.398	0.026	$-1.9 \cdot 10^{-4}$	$3.5 \cdot 10^{-6}$	$-5.9 \cdot 10^{-6}$
		45	-0.614	0.029	$-2.9 \cdot 10^{-4}$	$4.1 \cdot 10^{-6}$	$-1.5 \cdot 10^{-5}$
	Methanol	25	-0.591	0.028	$-1.6 \cdot 10^{-4}$	$3.9 \cdot 10^{-6}$	$-1.6 \cdot 10^{-5}$
		35	-0.835	0.037	$-4.8 \cdot 10^{-4}$	$5.8 \cdot 10^{-6}$	$1.2 \cdot 10^{-6}$
		45	-0.963	0.026	$-1.9 \cdot 10^{-4}$	$3.7 \cdot 10^{-6}$	$-8.0 \cdot 10^{-7}$
	Acetonitrile	25	-0.949	0.014	$2.8 \cdot 10^{-4}$	$1.2 \cdot 10^{-6}$	$-1.2 \cdot 10^{-5}$
		35	-1.159	0.022	$-3.5 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$	$-6.0 \cdot 10^{-6}$
		45	-1.096	0.011	$2.3 \cdot 10^{-4}$	$1.2 \cdot 10^{-6}$	$7.4 \cdot 10^{-7}$
BAT	Water	25	-0.531	0.062	$-1.3 \cdot 10^{-3}$	$1.2 \cdot 10^{-5}$	$7.8 \cdot 10^{-5}$
		35	-0.672	0.052	$-1.1 \cdot 10^{-3}$	$1.0 \cdot 10^{-5}$	$4.2 \cdot 10^{-5}$
		45	-0.904	0.057	$-1.2 \cdot 10^{-3}$	$1.1 \cdot 10^{-5}$	$4.7 \cdot 10^{-5}$
	Methanol	25	-0.705	0.037	$-2.9 \cdot 10^{-4}$	$4.3 \cdot 10^{-6}$	$-3.4 \cdot 10^{-6}$
		35	-0.845	0.038	$-4.1 \cdot 10^{-4}$	$5.1 \cdot 10^{-6}$	$-1.2 \cdot 10^{-6}$
		45	-0.863	0.031	$-3.1 \cdot 10^{-4}$	$4.5 \cdot 10^{-6}$	$-9.7 \cdot 10^{-6}$
	Acetonitrile	25	-1.137	0.038	$-9.2 \cdot 10^{-5}$	$2.7 \cdot 10^{-6}$	$-9.2 \cdot 10^{-6}$
		35	-1.211	0.035	$-7.4 \cdot 10^{-5}$	$2.5 \cdot 10^{-6}$	$-1.3 \cdot 10^{-6}$
		45	-1.266	0.032	$-5.0 \cdot 10^{-5}$	$2.1 \cdot 10^{-6}$	$1.5 \cdot 10^{-5}$
sBAT	Water	25	-0.585	0.070	$-1.7 \cdot 10^{-3}$	$1.5 \cdot 10^{-5}$	$-1.0 \cdot 10^{-4}$
		35	-0.792	0.067	$-1.5 \cdot 10^{-3}$	$1.4 \cdot 10^{-5}$	$-8.4 \cdot 10^{-5}$
		45	-0.845	0.058	$-1.3 \cdot 10^{-3}$	$1.3 \cdot 10^{-5}$	$6.9 \cdot 10^{-5}$
	Methanol	25	-0.417	0.028	$-8.9 \cdot 10^{-5}$	$3.5 \cdot 10^{-6}$	$-2.0 \cdot 10^{-5}$
		35	-0.726	0.035	$-3.3 \cdot 10^{-4}$	$5.2 \cdot 10^{-6}$	$-4.9 \cdot 10^{-6}$
		45	-1.003	0.041	$-3.9 \cdot 10^{-4}$	$5.0 \cdot 10^{-6}$	$2.1 \cdot 10^{-6}$
	Acetonitrile	25	-1.045	0.031	$4.7 \cdot 10^{-5}$	$2.5 \cdot 10^{-6}$	$-2.2 \cdot 10^{-5}$
		35	-1.241	0.039	$-2.2 \cdot 10^{-4}$	$4.3 \cdot 10^{-6}$	$-1.4 \cdot 10^{-5}$
		45	-1.163	0.029	$-1.1 \cdot 10^{-4}$	$3.6 \cdot 10^{-6}$	$-6.5 \cdot 10^{-6}$

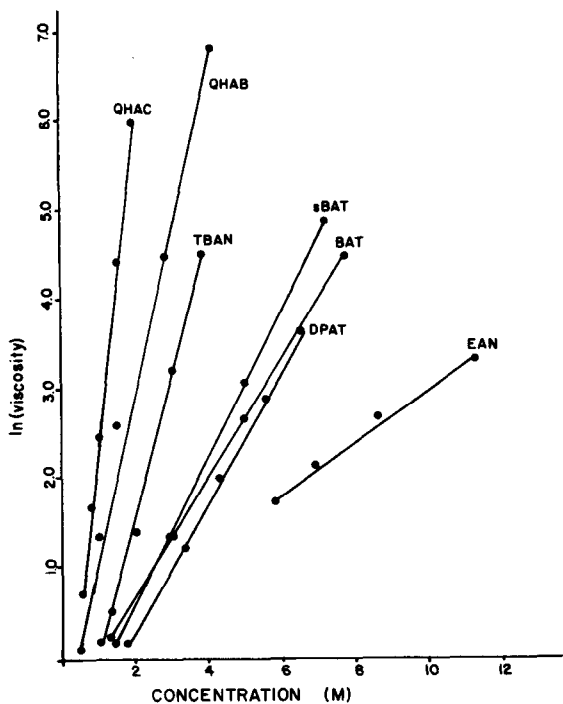


Fig. 6. Change in viscosity of liquid organic salts as a function of concentration in tetrahydrofuran at 25°C.

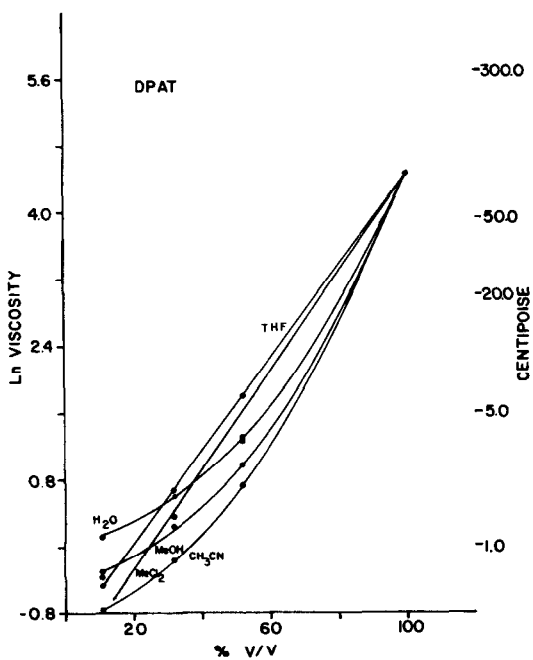


Fig. 7. Change in viscosity for DPAT as a function of the volume percent of DPAT in the diluting solvent at 25°C.

liquid salts into the range suitable for use in LC. By this means, mobile phases containing > 50% (v/v) of liquid salt could be used. The effect of increasing temperature on the viscosity of PAN solutions is shown in Fig. 8. Increasing the temperature decreases the viscosity of all solutions, but the effect is generally small.

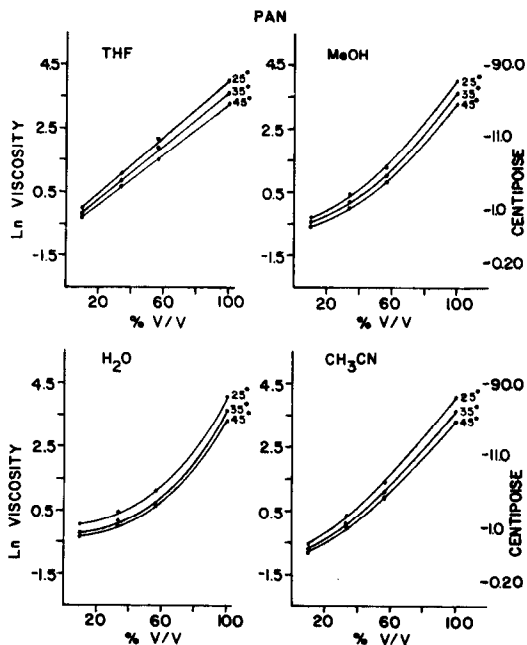


Fig. 8. Change in viscosity for PAN as the volume of diluting solvent and temperature is varied.

Because of the limited hydrolytic stability of silica-based reversed-phase column packings, an investigation of the pH of aqueous organic salt solutions was made. The aqueous solution pH values over the concentrations range 0.1–2.0 *M* for the liquid organic salts and some solid salts are summarized in Fig. 9. The concentration range studied for TBAN is somewhat shorter, due to its limited water solubility. The pK_a values for the alkylammonium cations are typically on the order of 10.5–11.0. From this, a solution pH of 5.0–6.0 would be anticipated for the concentration range studied. The acidity of all nitrate and thiocyanate salts studied is greater than that predicted from pK_a values, but for all liquid organic salts it is within the range tolerated by column packings. The higher acidity than predicted could only be accounted for by partial dissociation of the salt in aqueous solution. To eliminate the possibility of unintentional entrainment of nitric acid in the liquid salts as the reason for these observations, several crystalline salts were also dissolved in water, and their pH was measured. In general, the acidity of the solid and liquid salts is similar, and unintentional entrainment of acid in the liquid salts may be eliminated as a possible explanation of the results observed.

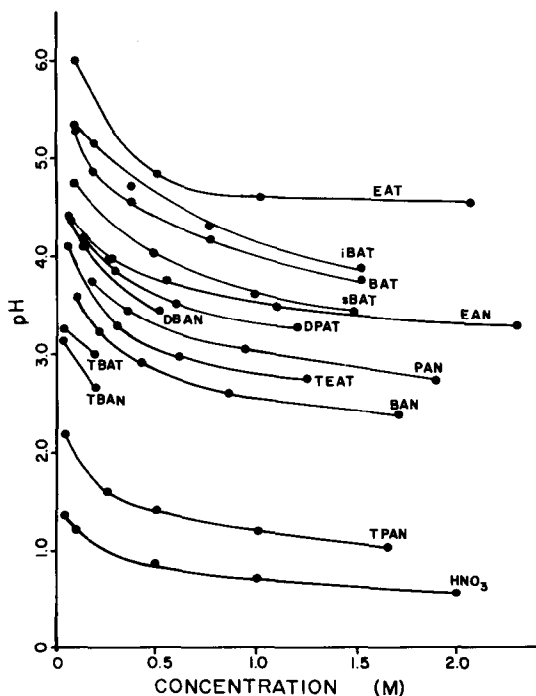


Fig. 9. Relationship between solution pH and concentration of organic salt. The solid salts used are identified in the legend to Fig. 5. IBAT = isobutylammonium thiocyanate.

CONCLUSIONS

The organic salts discussed in this study are air-stable liquids of moderate viscosity, suitable for use as selective solvents in analytical chemistry. When mixed with another solvent their viscosity is sufficiently low to permit their use as mobile phases in LC. As they form immiscible solvent pairs with solvents of low polarity, they are also suitable for use as stationary phases in liquid-liquid chromatography and as selective solvents for sample cleanup by liquid-liquid extraction.

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