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THERMODYNAMIC STUDY OF THE BEHAVIOUR OF TWO MOLTEN ORGANIC SALTS AS STATIONARY PHASES IN GAS CHROMATOGRAPHY

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(Received February 18th, 1987)

SUMMARY

The gas chromatographic retention behaviour of hydrocarbons of different types and of a group of halogenated compounds was measured at four temperatures from 20 to 30°C in columns containing ethylammonium nitrate (EAN) or *n*-propylammonium nitrate (PAN) as stationary phases. Thermodynamic functions of solution calculated from these data are compared to those in non-ionic organic solvents and in water. The solvent behaviour of both molten salts fits well with those of other solvents of high cohesive energy. Alkanes and olefins are retained by mixed processes of solution and adsorption at the gas-liquid interface.

INTRODUCTION

The chromatographic literature abounds with references to the use of molten salts, both inorganic and organic, as stationary phases. An excellent review has recently been published by Poole *et al.*¹

As a general rule, these phases have been selected in pursuit of either a high-temperature or a high-polarity separatory medium. Since organic compounds are sparingly soluble in molten inorganic salts, the selectivity of these stationary phases is rather poor. An organic cation or anion improves the solvent characteristics of the salt and allows a better control and greater variability of the salt properties.

Ethylammonium nitrate (EAN) melts at 14°C and exhibits as a solvent some similarities to water. Thus the critical micelle concentrations of surfactants in EAN are less than ten times larger than those in aqueous solutions², and the standard free energies, enthalpies and entropies for the transfer of rare gases and lower paraffins from the gas phase to EAN approach the values observed with water³. The cation in EAN has three hydrogen donor sites in a tetrahedral configuration and the anion has three acceptor sites in a planar configuration; the existence of an equal number of donor and acceptor sites and its high cohesive energy density⁴ strongly suggest that EAN, like water, may form a three-dimensional hydrogen-bonded network. Recent calorimetric measurements by Mirejovsky and Arnett⁵ have shown that the

heat capacities of solution, ΔC_{p2} , of the lower aliphatic alcohols in EAN (as well as in other highly associated solvents) are negligible in comparison with those in water. Water is unique in this sense, and its behaviour has been attributed⁶ to fluctuations of the water molecules between sites of different density and geometry; changes in temperature and the presence of foreign molecules disturb this fluctuating system.

Gas chromatography (GC) measures free energy as a function of temperature; enthalpies of solution are obtained from the first derivatives of the retention data with respect to temperature, and ΔC_{p2} values can be obtained from the second derivatives. The accuracy of the experimental data does not justify this second differentiation; non-ideal solution effects are obscured by gas-phase imperfection effects. The infinite dilution gas-liquid partition coefficients obtained by GC, however, are very reliable⁷ and constitute the best experimentally available free energy data to complement the enthalpies of solution measured by calorimetry; these, in turn, are markedly more accurate than the corresponding chromatographic results. Anyway, GC is very probably the best single technique for complete characterization of the thermodynamic behaviour of liquid mixtures.

On the basis of these arguments it was decided that a chromatographic investigation of systems involving EAN and a group of solutes of higher molecular weight than those studied by Evans *et al.*³ could furnish interesting information about the solvent properties of EAN. Some analytical applications of this molten salt as a stationary phase have been described by Poole and co-workers⁸. Our preliminary results led us to investigate also the homologous salt *n*-propylammonium nitrate (PAN).

EXPERIMENTAL

Materials

EAN was prepared by slowly adding 20% (v/v) nitric acid to a slight molar excess of a 33% (v/v) aqueous solution of ethylamine (Schuchardt), while stirring and cooling in an ice-water bath. The solution was concentrated in a rotary evaporator at 45–50°C, under a stream of nitrogen; the viscous and lightly yellow product thus obtained was passed through a column filled with charcoal, and the resulting colourless liquid was lyophilized twice, for 8 h each time. The water content, as determined by Karl Fischer titration, was 800 ppm and the melting point was about 14°C. PAN was prepared by the same method, using *n*-propylamine (UCB, Belgium); the melting point was about 5°C, and the water content was 1000 ppm.

Density values, measured by pycnometry, were fitted by the equations $D_t = 1.225 - 0.00063t$ for EAN and $D_t = 1.182 - 0.00066t$ for PAN, where t represents the temperature in °C. The surface tension of EAN at 25°C, interpolated from the data of Sugden and Wilkins⁹, is 47.9 dyn/cm; the value obtained for PAN in the present work by means of a Du Noüy tensiometer was 41.4 dyn/cm at 25°C.

Columns

Chromosorb W AW (60–80 mesh) was used as the solid support. Packings were prepared in a rotary evaporator, under a slow stream of nitrogen, using anhydrous methanol as the volatile solvent. In order to determine liquid surface effects, the following stationary phase concentrations were studied: 3.50, 6.02, 8.27, 10.07

TABLE I
THERMODYNAMIC FUNCTIONS OF SOLUTION IN EAN AT 25°C

| Compound | K_L | γ_1^∞ | $-\Delta H_k$ (kcal/mol) |
|-------------------------|-------|-------------------|--------------------------|
| <i>n</i> -Nonane | 21 | 2280 | 10.0 |
| <i>n</i> -Decane | 49 | 3080 | 11.4 |
| <i>n</i> -Undecane | 116 | 4190 | 12.1 |
| Benzene | 95.90 | 22.8 | 7.94 |
| Toluene | 161.7 | 45.2 | 8.92 |
| Ethylbenzene | 254.2 | 85.3 | 9.46 |
| <i>o</i> -Xylene | 396.2 | 78.4 | 9.75 |
| Chlorobenzene | 519.7 | 34.1 | 9.55 |
| <i>o</i> -Chlorotoluene | 762.6 | 75.6 | 10.51 |
| Carbon tetrachloride | 54.27 | 35.0 | 8.19 |
| Chloroform | 181.1 | 5.90 | 8.75 |
| Dichlorobromomethane | 502.8 | 6.30 | 9.33 |
| Dichloromethane | 96.72 | 4.94 | 7.62 |
| Bromochloromethane | 224.1 | 6.30 | 8.18 |

and 12.05% (w/w) of EAN, and 5.71, 10.49, 10.95 and 13.32% (w/w) of PAN. The free-flowing powders were packed by aspiration into 0.25 in. O.D. precoiled stainless-steel tubes, 0.5 or 1.0 m in length.

Apparatus and procedures

The equipment, techniques and procedures have been described elsewhere^{10,11}.

TABLE II
THERMODYNAMIC FUNCTIONS OF SOLUTION IN PAN AND LATENT HEATS OF CONDENSATION AT 25°C

| Compound | K_L | γ_1^∞ | $-\Delta H_k^*$ | $-\Delta H_L^*$ |
|-------------------------|-------|-------------------|-----------------|-----------------|
| <i>n</i> -Octane | 23 | 550 | 8.3 | 9.9 |
| <i>n</i> -Nonane | 45 | 913 | 9.5 | 11.1 |
| <i>n</i> -Decane | 89 | 1460 | 10.8 | 12.3 |
| <i>n</i> -Undecane | — | — | — | 13.5 |
| 1-Octene | 38 | 266 | 8.6 | 9.7 |
| 1-Nonene | 75 | 445 | 9.7 | 11.0 |
| 1-Decene | 144 | 757 | 10.8 | 12.2 |
| Benzene | 183.7 | 10.2 | 8.02 | 8.1 |
| Toluene | 354.2 | 17.6 | 9.01 | 9.1 |
| Ethylbenzene | 646.9 | 28.6 | 9.97 | 10.1 |
| <i>o</i> -Xylene | 694.4 | 38.2 | 10.18 | 10.4 |
| Chlorobenzene | 1264 | 11.9 | 10.14 | 10.2 |
| <i>o</i> -Chlorotoluene | 2147 | 22.9 | 10.77 | 10.9 |
| Carbon tetrachloride | 103.5 | 15.7 | 8.01 | 7.9 |
| Chloroform | 299.5 | 3.04 | 8.69 | 7.4 |
| Dichlorobromomethane | 854.9 | 3.16 | 9.67 | 8.5 |
| Dichloromethane | 135.1 | 3.02 | 7.53 | 6.8 |
| Bromochloromethane | — | — | — | 7.9 |

* Units: kcal/mol.

TABLE III
 ADSORPTION COEFFICIENTS ($K_A \cdot 10^4$ cm) AT 25°C

| Compound | EAN | PAN |
|--------------------|------|------|
| <i>n</i> -Octane | — | 4.71 |
| <i>n</i> -Nonane | 10.8 | 11.7 |
| <i>n</i> Decane | 26.7 | 28.4 |
| <i>n</i> -Undecane | 58.6 | — |
| 1-Octene | — | 5.31 |
| 1-Nonene | — | 12.7 |
| 1-Decene | — | 31.0 |

Analytical grade nitrogen, previously purified by passing through a molecular sieve (Davidson 5A) trap, was used as the carrier gas, at flow-rates between 15 and 60 cm³/min, in accord with the solute retention behaviour. Each column was preconditioned by passing through it a small flow of nitrogen, at 30°C, for 24 h. Retention times were measured at four temperatures within the range 20–30°C. Solutes were injected, together with a small sample of methane, by means of 10- μ l Hamilton syringes, applying the headspace sampling technique; the sample size was of the order of 10⁻² μ mol, the resulting peaks displaying an excellent symmetry. For each solute-column-temperature combination, the retention time was the mean of not less than three injections. Adjusted times were measured between the methane peak and the maximum of the solute peak.

RESULTS

The retention volumes were calculated in the usual form¹² from the adjusted retention times and operating conditions. With the exception of those for the alkanes and the olefins, plots of the retention volume per gram of packing against the percentage of stationary phase are straight lines through the origin, indicating that for these solutes, within experimental error, retention is due exclusively to gas-liquid partitioning. For alkanes and olefins, in columns containing EAN or PAN as the stationary phase, these plots show that chromatographic retention results from the effects both of partition and adsorption at the gas-liquid interface¹³.

In the case of solutes retained by mixed mechanisms, the gas-liquid partition coefficients, K_L , and the adsorption coefficients, K_A , were obtained according to Martin^{14,15}, in the form detailed in a previous publication¹⁶. Partition coefficients for solutes retained exclusively by dissolution in the stationary phase were calculated by means of the relationship $K_L = V_N/V_L$, where V_N and V_L represent the net retention volume and the liquid phase volume in the most heavily loaded column.

Standard partial molar free energies, ΔG_k° , enthalpies, ΔH_k° , and entropies, ΔS_k° , of solution, corresponding to the transfer of 1 mol of solute from an ideal vapour phase at a pressure of 1 atm to an hypothetical solution at unit molar fraction and obeying Henry's law, were calculated from the values of K_L and their dependence on temperature, as previously described^{16,17}. The thermodynamic properties reported for solutes retained by mixed mechanisms are markedly more uncertain than those for non-adsorbed solutes; when the errors in ΔH_k° are computed according to the

method proposed¹⁸, standard deviations between 0.5 and 1.5% are found for solutes retained exclusively by solution, 4–6% for alkanes and olefins in PAN and up to 30% for alkanes in EAN.

The activity coefficients at infinite dilution were calculated by the well known equation

$$\gamma_1^\infty = RT/p_1^*v_2K_L^\infty \quad (1)$$

where p_1^* represents the vapour pressure of the pure solute and v_2 is the molar volume of the stationary phase. The solution properties in EAN and in PAN are summarized in Tables I and II, respectively; the latent heats of condensation at 25°C, ΔH_L^∞ , are also included in Table II. Both p_1^* and ΔH_L^∞ were taken from Dreisbach's compilation^{19–21}. The adsorption coefficients at 25°C in both stationary phases are given in Table III.

DISCUSSION

It is usually accepted that adsorption at the gas–liquid interface is important for solutes with large positive deviations from the ideal behaviour, in high-surface-tension stationary phases. Strong adsorption effects could be predicted on this basis for all the solutes studied in the present investigation, particularly when their activity coefficients in EAN or PAN and surface tensions of the molten salts are compared with the respective values in systems involving other stationary phases of high cohesive energy density^{10,11,16,22,23}. However, only the alkanes and the olefins show detectable adsorption, thus corroborating the difficulties in predicting the behaviour of surface phases from the bulk properties of the mixtures²². The adsorption coefficients of *n*-nonane and *n*-decane in the two stationary phases studied here, for instance, are almost coincident, but the values of the activity coefficients in EAN are twice as high as those in PAN.

Positive deviations from the ideal solution behaviour decrease in the order alkanes > olefins > aromatics > halomethanes; for a given solute, the infinite dilution activity coefficient in EAN is about twice that in PAN.

Partial molar excess properties of solution can be calculated by means of the equations:

$$\overline{\Delta G_1^E} = RT \ln \gamma_1^\infty \quad (2)$$

$$\overline{\Delta H_1^E} = \Delta H_k^\infty - \Delta H_L^\infty \quad (3)$$

$$\overline{\Delta S_1^E} = (\Delta H_1^E - \Delta G_1^E)/T \quad (4)$$

$\overline{\Delta H_1^E}$ is positive for hydrocarbons of any type in both stationary phases; however, the enthalpic contributions represent only 20–40% of the large positive excess free energies for alkanes and olefins, and 5–10% in the case of aromatic hydrocarbons. There-

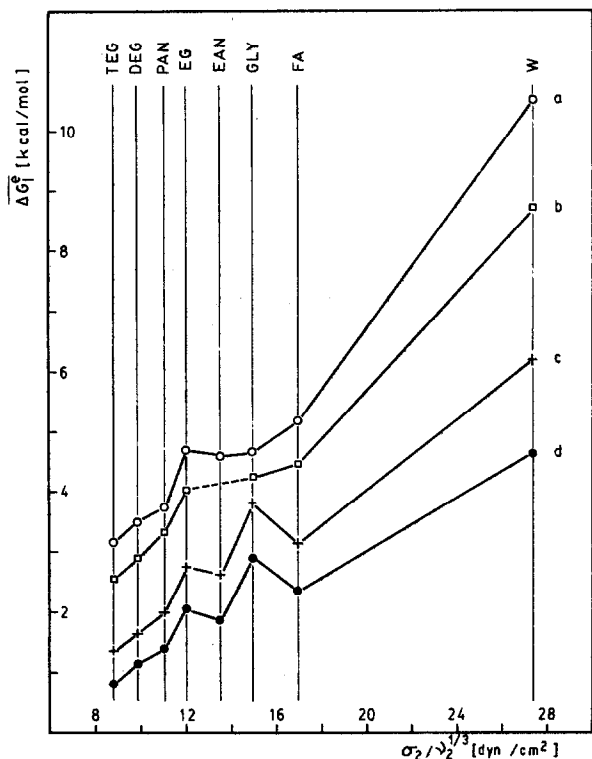


Fig. 1. Plots of the partial molar excess free energy, ΔG_1^e , against the quotient $\sigma_2/v_2^{1/3}$, where σ_2 and v_2 represent the surface tension and molar volume of the solvent, respectively. Solutes: a, *n*-nonane; b, 1-octene; c, ethylbenzene; d, benzene. Solvents and data sources: TEG and DEG = tri- and diethylene glycol¹¹; EG = ethylene glycol²³; GLY = glycerol¹⁶; FA = formamide¹⁶; W = water²⁶.

fore, the low solubilities of hydrocarbons in the molten salts result mainly from large entropy losses in the mixing process. The excess enthalpies for the halomethanes are negative but, again, large negative entropic contributions give rise to positive deviations from the ideal behaviour; however, with the exception of carbon tetrachloride, their infinite dilution activity coefficients are markedly lower than those for the hydrocarbons.

One reason for our interest in the solvent properties of EAN was the findings, by Evans *et al.*³, that the standard free energies of solution for krypton and the lower alkanes were more positive than in any other non-aqueous solvent, becoming less positive as the alkane molar volume decreases. Following Mirejovsky and Arnett⁵, the standard partial molar excess free energies of solution at 25°C for hydrocarbons of different types in EAN, PAN, water and in several highly associated organic solvents have been plotted in Fig. 1 as a function of $\sigma_2/v_2^{1/3}$, where σ_2 is the surface tension of the solvent and v_2 its molar volume. The cohesive energy density is given most conveniently by the Hildebrand solubility parameter, defined as $(\Delta E_v/v_2)^{1/2}$, where ΔE_v is the energy of vaporization of the solvent; since ΔE_v is not accessible for ionic liquids, the quantity $\sigma_2/v_2^{1/3}$, shown by Hildebrand and Scott²⁵ to be closely

related to the solubility parameter, was proposed by Gordon⁴ as an alternative measure of cohesion for molten salts.

The excess free energies in the molten salts are smaller than those obtained in formamide, ethylene glycol or glycerol; from this point of view, these three solvents bear a stronger resemblance to water than do either EAN or PAN. Furthermore, the

ΔG_1° values in both salts correlate well with those in the organic solvents and in water. In our opinion, the low solvent power of this group of liquids towards the hydrocarbons is due to their high cohesive density, and there is nothing special in this respect about the solvent behaviour of the molten salts.

These behaviours were examined more closely by comparing the values of the other thermodynamic properties of solution; ΔG_k° , ΔH_k° and $T\Delta S_k^{\circ}$ values for three aromatic hydrocarbons in the aforementioned solvents are plotted separately in Fig. 2. The values of the enthalpies of solution in EAN, in PAN or in water are very similar, and more negative than those in other solvents. The entropies of solution in

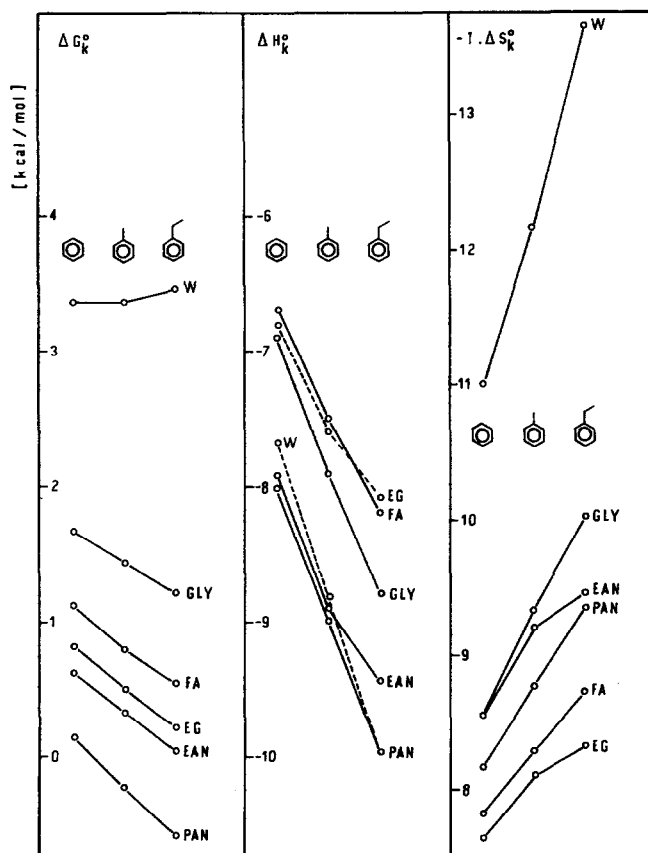


Fig. 2. Standard partial molar free energies, ΔG_k° , enthalpies, ΔH_k° , and the product between the temperature and standard partial molar entropy, $T\Delta S_k^{\circ}$, for benzene, toluene and ethylbenzene in several solvents at 25°C. Solvent symbols and data sources as in Fig. 1.

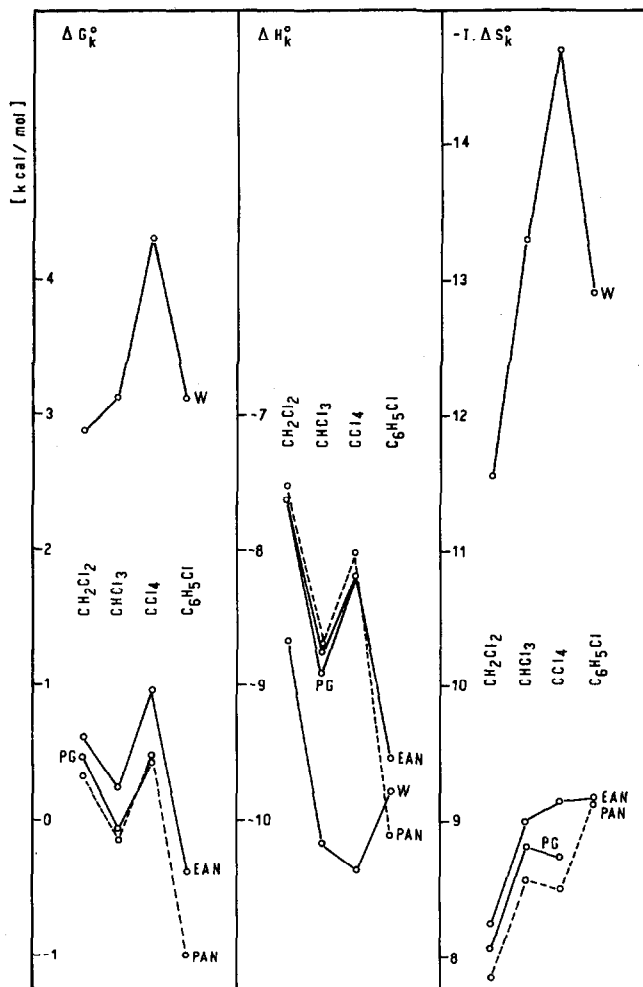


Fig. 3. Plots as in Fig. 2 for several chlorinated solutes in several solvents at 25°C.

water, however, are markedly more negative than those in any other solvent. In the case of the chlorinated solutes, the same type of plot (see Fig. 3) indicates that the very large entropy loss in the solution process is the most important difference between water and the remaining solvents; the behaviours of both molten salts follow closely that of propylene glycol.

On the basis of the experimental evidence reported, it can be stated that the behaviour of both molten salts in the presence of non-polar or moderately polar solutes shows no important differences in relation to that of other non-ionic solvents of high cohesive energy density. In our opinion it is not possible to assign to EAN an intermediate position between water and ordinary non-aqueous solvents. In accord with current thinking, large heat capacities of solution constitute the most important criterion for discriminating between water and the remaining solvents; how-

ever, the experimental data gathered in the present paper show that it is not possible to ignore the large entropy losses associated with the solution of non-polar solutes in water, and water can be considered as an unique liquid, as pointed out by Frank and Evans²⁷ more than 40 years ago.

ACKNOWLEDGEMENTS

This work was sponsored by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and by the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC).

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