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THERMOCHEMICAL INVESTIGATIONS OF GAS-LIQUID CHROMATOGRAPHY

III. RETENTION BEHAVIOR OF ALKANE SOLUTES ON BINARY LIQUID CRYSTALLINE SOLVENT MIXTURES

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SUMMARY

Retention volumes have been determined for *n*-heptane, *n*-octane, and *n*-nonane on binary butyl *p*-(*p*-ethoxyphenoxy-carbonyl)phenyl carbonate and *p*-(*p*-ethoxyphenylazo)phenyl undecylenate liquid crystalline stationary phases from 60 to 90°C. Results of these measurements are used to calculate enthalpies, entropies, and free energies of solution at the six solvent compositions studied. The three enthalpy and entropy of solution curves show pronounced minimum values near an equimolar mixture of the two stationary phases. The Gibbs free energies of solution, in comparison, are linear or nearly linear with solvent composition.

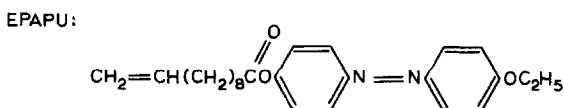
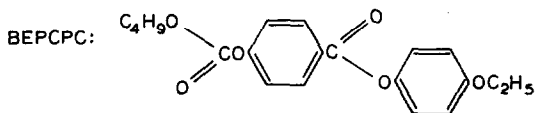
INTRODUCTION

During the past decade, gas-liquid chromatography (GLC) has proven to be an accurate and convenient method for measuring vapor-liquid equilibria data for non-electrolyte systems. This is particularly true in the low concentration regions (infinite dilution) normally inaccessible by conventional static vapor pressure techniques. The data generally obtained include the chromatographic partition coefficient K_R and the Raoult's law activity coefficients of the volatile solute (component A) at infinite dilution γ_A^∞ in the stationary liquid phase.

Binary liquid mixtures have also been investigated by a large number of individuals. There are two main purposes of this type of investigation. The first is an attempt to control the selectivity of a chromatographic column through the use of mixed liquid phases, and the second is an attempt to measure precise thermodynamic data for testing theories of non-electrolyte solutions.

Thermodynamic GLC studies, for the most part, have been limited to stationary phases of either pure components or binary mixtures of isotropic liquids. Systematic investigations and comparative studies on binary liquid crystalline solvent are lacking. In this paper we report the retention behavior of *n*-heptane, *n*-octane, and *n*-nonane on binary butyl *p*-(*p*-ethoxyphenoxy-carbonyl)phenyl carbonate

(BEPCPC) and *p*-(*p*-ethoxyphenylazo)phenyl undecylenate (EPAPU) liquid crystalline solvent mixtures at temperatures between 60 and 90°C. The phase diagram determined by Berheim and Shuhler¹ indicates that, at the temperatures studied, mixtures of EPAPU and BEPCPC exist as a nematic liquid crystalline phase over the entire range of binary composition.



EXPERIMENTAL

Chemicals

n-Heptane, *n*-octane, and *n*-nonane were used as received from Aldrich (Gold Label). BEPCPC, purchased from Eastman-Kodak, was recrystallized once from 95% ethanol. EPAPU was synthesized in two steps via esterification of a diazo-coupling product.

Preparation of diazo-couple

p-(*p*-Ethoxyphenylazo)phenol was prepared by coupling diazonium chloride and phenolate. Diazonium chloride was made by slowly (1 ml/min) adding a sodium nitrite solution (27.5 g in 250 ml of water) to a cooled (less than 0°C) mixture of *p*-phenetidine (Aldrich, 50 g, 0.365 mol) in 150 ml of 6 *F* hydrochloric acid. The phenolate was made by the addition of 34.5 g (0.365 mol) of phenol to 38.5 g (0.365 mol) of sodium carbonate in 350 ml of water. The coupling product was prepared by slowly adding the diazonium chloride to the ice-cooled phenolate. The golden-yellow product was dried and the recrystallized three times from benzene. Recrystallized yield was 58.9 g (66.6%, m.p. 114°C).

Preparation of the EPAPU ester

To 4.00 g (16.52 mmol) of the *p*-(*p*-ethoxyphenylazo)phenol dissolved in 15 ml of ice-cold pyridine in a flask flushed with nitrogen, were added slowly by syringe 25 mmol of undecylenoate chloride. The resulting mixture was stirred for several hours in an ice-bath, then added to 100 ml of ice-cold 1 *M* sulfuric acid, collected, washed with 200 ml of cold water, and subsequently recrystallized three times from ethanol. The purified ester (60% yield) was a yellow crystalline solid (m.p. 63°C, in good agreement with the literature value²).

Apparatus

The gas chromatograph was a Varian Model 3700 equipped with dual hydrogen flame ionization detectors. Injection port and detector temperatures were main-

tained at 200°C. Column temperatures, maintained constant to $\pm 0.2^\circ\text{C}$, were read direct from the digital readout which was calibrated against an NBS thermometer. The hydrogen flow-rate was maintained at 30 ml/min and the air flow-rate at 300 ml/min. The nitrogen carrier gas was passed through a molecular sieve moisture trap and the flow-rates were measured by a soap film flowmeter at each column temperature (accurate to 0.001 ml/min). A Spectro-Physics Model 4270 integrator was used to monitor elution with retention time accuracy of 0.1 second.

Preparation of columns.

Pure and mixed liquid crystalline solids were deposited onto Chromosorb P (100–120 mesh, acid-washed and DMSC-treated) from solution in diethyl ether. The volatile solvent was removed by rotary evaporation and the resultant free-flowing powders were packed by aspiration into 6 ft. \times 1/8 in. O.D. stainless-steel tubing. A 20% (w/w) coating was chosen as the loading percentage to eliminate surface effects and to insure a liquid crystalline stationary phase^{3,4}.

Procedure

For each solvent, retention times were measured in triplicate at 5–10°C intervals over the range 60–90°C. Each column was tested at least five times over a one-week period to ensure reproducibility of retention measurements, column temperatures and flow-rates. Solutes were injected using a microliter Hamilton syringe.

RESULTS AND DISCUSSION

Thermodynamic properties of solution for *n*-heptane, *n*-octane, and *n*-nonane were derived according to the following equations⁵:

$$\Delta G = -RT \ln (MV_g/273R)$$

$$\Delta H = -R [d \ln V_g/d(1/T)]$$

$$\Delta S = (\Delta H - \Delta G)/T$$

where *M* is the average molecular weight of the solvent, *V_g* is the specific retention volume and the remaining symbols having their usual meanings. Calculated properties refer to the transfer of the solute in the gas phase, at temperature *T*, atmospheric pressure and behaving ideally, into the liquid crystalline solvent at temperature *T*, solute mole fraction equal to unity, but with molecular interactions characteristic of infinite dilution. Enthalpies, entropies, and free energies of solution are shown in Figs. 1–3 as a function of stationary phase composition. Estimated uncertainties are 2–4% of the reported value.

Inspection of Figs. 1–3 reveals that the three entropy and enthalpy curves show pronounced minimum values between BEPCPC concentrations of 0.40 and 0.50 mole fraction. The free energy curves, on the other hand, show only a slight non-linearity with solvent composition. The nearly linear free energy curves result because of compensation between the enthalpic and entropic contributions. A comprehensive thermodynamic model for alkane solutes on binary liquid crystalline stationary phases must be capable of describing not only the near-linear Gibbs free energy of solution, but also the pronounced minima in the enthalpy and entropy of solution curves. It

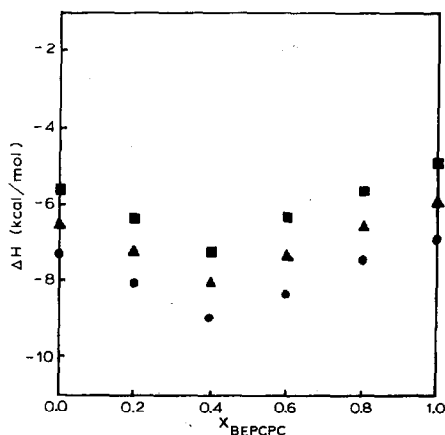


Fig. 1. Enthalpies of solution for *n*-heptane (■), *n*-octane (▲), and *n*-nonane (●) as a function of stationary phase composition.

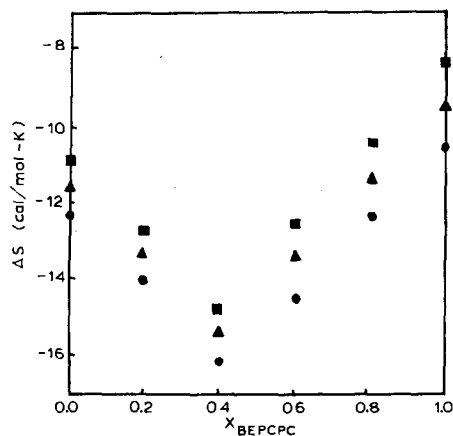


Fig. 2. Entropies of solution for *n*-heptane (■), *n*-octane (▲), and *n*-nonane (●) at 343 K as a function of stationary phase composition.

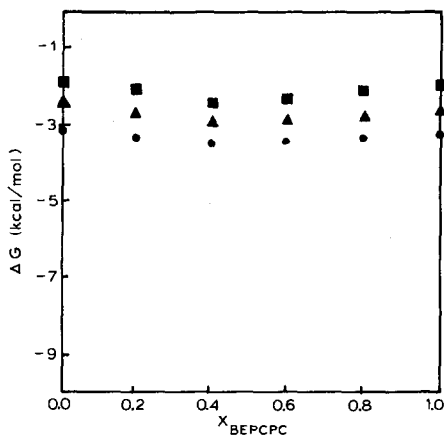


Fig. 3. Gibbs free energies of solution for *n*-heptane (■), *n*-octane (▲), and *n*-nonane (●) at 343 K as a function of stationary phase composition.

is premature at this point to propose a thermodynamic model after studying the retention behavior of only three alkane solutes. Results of this study do suggest, however, that the microscopic partition model⁶⁻⁸ may not be appropriate for describing the thermodynamic properties of a solute on binary liquid crystalline phase. The microscopic partition model does not give an extremum in the enthalpy of solution curve⁹.

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