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Thermodynamic Properties of Dilute Solutions of C_2–C_6 *n*-Alkanoic Acids in Sulfolane

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Partial molar volumes, $\bar{v}_2$, of the first five members of the *n*-alkanoic acid series in dilute sulfolane solutions were measured at 303.16 K. Cryoscopic measurements were also carried out on propionic acid–sulfolane solutions in equilibrium with disordered crystal I. Both sets of experimental data suggest that interactions between the dissolved acid and sulfolane are of limited importance. Cryoscopic measurements further indicate that the dissolved acid does not dimerize or dissociate in these solutions. A partition of the acid between the disordered crystal I and liquid sulfolane solutions is suggested, however, and the partition coefficient is calculated from the cryoscopic measurements. Experimental data on volumes are analyzed in the light of current theories based on group contribution models and the COOH group contribution is calculated.

Introduction

Previously (*1*, *2*) we reported the results of some density measurements carried out on C_2–C_5 normal and branched alkanenitriles, in the pure state and in aqueous and nonaqueous solutions, with the aim of deriving the CN group contribution. On that occasion we illustrated a method for calculating the void volume of molecules, responsible for interactions of any kind, and proposed some criteria for evaluating the extent of solute–solute and solute–solvent interactions.

We provide herewith a new contribution for testing the adequacy of theory, by determining the partial molar volumes, $\bar{v}_2$, of C_2–C_6 *n*-alkanoic acids in dilute sulfolane solutions. This study allows us to calculate the COOH group contribution directly, as the dissolved acid neither dissociates nor dimerizes in sulfolane (the dissociation is indeed a feature of protic solvents, the association to molecular pairs of apolar solvents); sulfolane (*3*) is an aprotic solvent with a moderately high dielectric constant. With the aim of supporting the above statement, cryoscopic measurements are carried out on propionic acid–sulfolane solutions in equilibrium with disordered crystal I.

Experimental Section

Materials. Sulfolane kindly supplied by Shell Italia was carefully purified and dried as previously reported (*4*).

Carlo Erba RPE *n*-alkanoic acids were purified as recommended by Vogel (*5*). Acetic acid was partially frozen—about one-half was discarded as unfrozen liquid—and then fractionally distilled from potassium permanganate. Propionic, butyric, valeric, and caproic acids were repeatedly distilled over anhydrous sodium sulfate and then over potassium permanganate.

Physical properties of the purified materials are in good agreement with the most reliable literature data (*6*–*9*).

Solutions were prepared by weight (reduced to mass) in a drybox. Compositions are stated as molality of acid, *m*; the acids are indicated as component 2. Densities ($d_{1,2}$) are given in units of g·cm^{-3} and volumes (ϕ_2 and $\bar{v}_2$) in cm^3·mol^{-1}.

Apparatus. Densities were measured at 303.16 K with a DMA 60 vibrating-tube digital precision densimeter (Anton Paar, Austria). The apparatus and the temperature-controlling equipment were described elsewhere (*10*). The maximum error in density did not exceed 1×10^{-5} g·cm^{-3}. For each system densities were measured at different compositions ranging from 0.001 to 0.028 *m*.

Cryoscopic measurements on solutions were carried out by using the cryoscopic apparatus described elsewhere (*11*). Temperatures were measured with a NBS certified platinum resistance thermometer assembled with a G2 Model Müller bridge. The precision in temperature was 0.001 K. Both cooling and heating curves were taken; in the case of cooling curves the initial freezing points were determined by extrapolation across the undercooling region. Agreement between the initial freezing temperature and the final melting temperature of each solution was usually within 0.005 K.

Results

Densities. Experimental values of density $d_{1,2}^{303.16\text{K}}$ and molalities, *m*, of selected dilute C_2–C_6 *n*-alkanoic acid–sulfolane

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Table I. Densities ($d_{1,2}$) and Volumes ($V_{1,2}$)[a] of Sulfolane (1)–Acetic Acid (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 303.16 K

m[c]	$d_{1,2}$[d]	$V_{1,2}$[e]	ϕ_2[f]	$\bar{v}_2$[f]
0.000 00	1.262 28	792.217		
0.002 65	1.262 24	792.368	56.981	56.604
0.005 83	1.262 19	792.551	57.290	57.118
0.007 75	1.262 17	792.655	56.516	56.387
0.011 08	1.262 13	792.839	56.137	56.047
0.015 39	1.262 05	793.094	56.985	56.920
0.020 94	1.261 98	793.402	56.590	56.543
0.025 72	1.261 91	793.674	56.649	56.610

[a] $V_{1,2} = 792.218 + 56.624m$ (eq 2). [b] Solvent = sulfolane; solute = acetic acid. [c] Molality. [d] Units: g·cm^{-3}. [e] Units: cm^3. [f] Units: cm^3·mol^{-1}.

Table II. Densities ($d_{1,2}$) and Volumes ($V_{1,2}$)[a] of Sulfolane (1)–Propionic Acid (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 303.16 K

m[c]	$d_{1,2}$[d]	$V_{1,2}$[e]	ϕ_2[f]	$\bar{v}_2$[f]
0.000 00	1.262 40	792.142		
0.005 20	1.262 27	792.529	74.423	74.423
0.007 19	1.262 23	792.671	73.574	73.574
0.010 79	1.262 14	792.938	73.772	73.772
0.013 11	1.262 09	793.106	73.532	73.532
0.015 73	1.262 03	793.293	73.172	73.172
0.015 81	1.262 03	793.302	72.371	73.371
0.016 98	1.262 00	793.390	73.498	73.498
0.044 46	1.261 35	795.413	73.572	73.572

[a] $V_{1,2} = 792.142 + 73.521m$ (eq 2). [b] Solvent = sulfolane; solute = propionic acid. [c] Molality. [d] Units: g·cm^{-3}. [e] Units: cm^3. [f] Units: cm^3·mol^{-1}.

Table III. Densities ($d_{1,2}$) and Volumes ($V_{1,2}$)[a] of Sulfolane (1)–Butyric Acid (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 303.16 K

m[c]	$d_{1,2}$[d]	$V_{1,2}$[e]	ϕ_2[f]	$\bar{v}_2$[f]
0.000 00	1.262 31	792.198		
0.004 95	1.262 13	792.657	92.727	91.255
0.008 00	1.262 03	792.933	91.875	90.964
0.009 29	1.262 00	793.042	90.850	90.066
0.013 70	1.261 86	793.438	90.511	89.979
0.015 33	1.261 80	793.589	90.737	90.262
0.018 17	1.261 71	793.844	90.589	90.188
0.021 74	1.261 60	794.163	90.386	90.051
0.023 16	1.261 55	794.293	90.458	90.143

[a] $V_{1,2} = 792.205 + 90.164m$ (eq 2). [b] Solvent = sulfolane; solute = butyric acid. [c] Molality. [d] Units: g·cm^{-3}. [e] Units: cm^3. [f] Units: cm^3·mol^{-1}.

Table IV. Densities ($d_{1,2}$) and Volumes ($V_{1,2}$)[a] of Sulfolane (1)–Valeric Acid (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 303.16 K

m[c]	$d_{1,2}$[d]	$V_{1,2}$[e]	ϕ_2[f]	$\bar{v}_2$[f]
0.000 00	1.262 22	792.255		
0.002 63	1.262 11	792.537	107.224	106.464
0.005 21	1.262 00	792.815	107.486	107.102
0.007 72	1.261 89	793.087	107.772	107.513
0.010 36	1.261 78	793.370	107.625	107.432
0.012 99	1.261 67	793.652	107.544	107.390
0.017 19	1.261 49	794.105	107.621	107.504
0.027 58	1.261 07	795.211	107.179	107.107

[a] $V_{1,2} = 792.257 + 107.253m$ (eq 2). [b] Solvent = sulfolane; solute = valeric acid. [c] Molality. [d] Units: g·cm^{-3}. [e] Units: cm^3. [f] Units: cm^3·mol^{-1}.

Table V. Densities ($d_{1,2}$) and Volumes ($V_{1,2}$)[a] of Sulfolane (1)–Caproic Acid (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 303.16 K

m[c]	$d_{1,2}$[d]	$V_{1,2}$[e]	ϕ_2[f]	$\bar{v}_2$[f]
0.000 00	1.262 27	792.224		
0.002 70	1.262 13	792.554	122.222	122.963
0.008 21	1.261 86	793.237	123.386	123.630
0.011 43	1.261 70	793.634	123.360	123.535
0.014 24	1.261 56	793.981	123.385	123.525
0.016 34	1.261 43	794.256	124.357	124.480
0.019 57	1.261 28	794.648	123.849	123.965
0.022 00	1.261 16	794.947	123.773	123.864
0.025 93	1.260 97	795.429	123.602	123.679

[a] $V_{1,2} = 792.222 + 123.854m$ (eq 2). [b] Solvent = sulfolane; solute = caproic acid. [c] Molality. [d] Units: g·cm^{-3}. [e] Units: cm^3. [f] Units: cm^3·mol^{-1}.

Table VI. Volume ($V_2°$) of Pure n-Alkanoic Acids and Partial Molar Volumes ($\bar{v}_2$) in Sulfolane Solution at 303.16 K[a]

substance	$d_2°$/ (g·cm^{-3})	$V_2°$/ (cm^3·mol^{-1})	$\bar{v}_2$/ (cm^3·mol^{-1})
acetic acid	1.043 02	57.576	56.624
propionic acid	0.983 35	75.334	73.521
butyric acid	0.947 75	92.964	90.164
valeric acid	0.929 62	109.866	107.253
caproic acid	0.918 75	126.434	123.854

[a] $V_2° = 57.985 + 17.225n(\mathrm{CH_2})$; $\bar{v}_2 = 56.645 + 16.819n(\mathrm{CH_2})$.

Table VII. Molalities (m) of Dilute Solutions of Propionic Acid in Sulfolane, Initial Freezing Points (fp), Experimental Molar Depressions (θ/m), Ideal Solution Molar Depressions ($(\theta/m)_i$), and Partition Coefficients (K)

m	fp, °C	θ/m	$(\theta/m)_i$	$1 - K$
0.0000	28.450		65.000	
0.0105	27.856	56.571	64.813	0.873
0.0177	27.480	54.802	64.685	0.847
0.0260	27.034	54.462	64.538	0.844
0.0365	26.460	54.521	64.353	0.847
0.0407	26.162	56.216	64.279	0.878
0.0509	25.737	53.301	64.101	0.832
0.0595	25.182	54.924	63.952	0.859
0.0795	24.104	54.667	63.607	0.859
0.1039	22.848	53.917	63.191	0.853
0.1440	20.781	53.257	62.520	0.852
0.1853	18.558	53.383	61.844	0.863

solutions are summarized in Tables I–V, where also the average density $d_1^{303.16\mathrm{K}}$ of the solvent, before and after each run, is reported; from molalities and densities the volumes $V_{1,2}$ of solutions were calculated and the apparent volume of the solute was derived, at each composition, by using the equation

$$\phi_2 = (V_{1,2} - 1000/d_1)/m \qquad (1)$$

In the selected molality range ϕ_2 values do not depend on dilution; therefore, the partial molar volumes $\bar{v}_2 = (\delta V_{1,2}/\delta n_2)_{n_1}$ of the solute could be calculated by smoothing an equation of the type

$$V_{1,2} = (1000/M_1)\,\bar{v}_1 + \bar{v}_2 m \qquad (2)$$

where M_1 is the molar weight and $\bar{v}_1$ the partial molar volume of the solvent; the last is obtained on extrapolation of eq 2 at $m = 0$. Tabulated in Tables I–V are also volumes of the various solutions calculated from eq 2, which reproduces experimental values of volume and hence of density within the limits of experimental error. All volumes $V_2°$ and $\bar{v}_2$ of acids are summarized in Table VI. Both volume $V_2°$ and partial molar volume, $\bar{v}_2$, in sulfolane solutions exhibit a linear dependence on the number of $\mathrm{CH_2}$ groups in the acid molecule. This behavior is represented by the equations

$$V_2° = 57.985 + 17.225n(\mathrm{CH_2}) \qquad (3)$$

$$\bar{v}_2 = 56.645 + 16.819n(\mathrm{CH_2}) \qquad (4)$$

Table VIII. Volumes ($V_2°$), Vaporization Enthalpies (ΔH_v) at 298.16 K and T_B, and van der Waals Volumes (v_w)[a] of Selected Acids

substance	$V_2°_{298.16K}$/ (cm^3·mol^{-1})	$\Delta H_v^{298.16K}$/ (kcal·mol^{-1})	$\Delta H_v^{T_B}$/(kcal·mol^{-1}) a	b	c[b]	v_w/(cm^3·mol^{-1})
acetic acid	57.541	12.49	5.825	8.994	8.927	33.56
propionic acid	74.980	13.70	9.526	9.522	9.551	44.18
butyric acid	92.433	15.20	10.040	10.038	10.152	55.42
valeric acid	109.293	16.56	10.53	10.549	10.746	66.28
caproic acid	125.852	17.00		11.014	11.289	75.63

[a] $v_w = 33.77 + 10.62n(CH_2)$ (eq 8). [b] n_D from ref *18*.

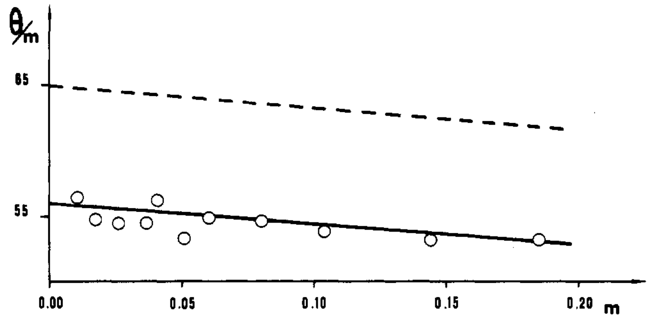

Figure 1. Plots of the molar depressions of solvent (sulfolane) freezing point, θ/m, vs. solute (propionic acid) molality, m: ideal values (dashed line) and experimental points (open circles).

Cryoscopic Measurements. Table VII and Figure 1 summarize the results of some cryoscopic measurements carried out, in the molality range 0–0.2 m, for sulfolane solutions of propionic acid in equilibrium with disordered crystal I. The magnitude of molar depressions, steadily decreasing with molality, allows us to exclude both dissociation of acid to ions or association to molecular pairs. They do not gain on extrapolation at $m = 0$, the value of cryoscopic constant, $\lambda_1 = 65$ K·kg·mol^{-1}, of the sulfolane solutions in equilibrium with crystal I. This may be interpreted in terms of a partition of solute between solid and liquid phases as observved in the case of our previous cryoscopic measurements (*12*) on selected solutes and by Husar and Creevoy (*13*) in the case of trifluoroacetic acid–sulfolane solutions. In the last column the partition coefficient of the acid, at each molality, has been calculated on the basis of the actual molar depressions and the ideal molar depressions calculated with

$$(\theta/m)_i = 65 - 17.914m + 5.015m^2 - 1.409m^3 \qquad (5)$$

(dashed line in Figure 1). Equation 5 was derived by one of us (*11*) from sulfolane thermal data on the supposition that the specific heat of the disordered crystal I does not differ noticeably from the specific heat of the liquid phase. The constant value of the ratio $(\theta/m)/(\theta/m)_i = 1 - k$, in the last column of Table VII, is indicative of the validity of our interpretation.

Discussion

Both values of CH_2 group increments, at 303.16 K, for pure substances (17.235) and for dilute sulfolane solutions (16.825) are in good agreement with our previous data which refer to the C_2–C_8 normal nitrile series (17.11 and 16.70, respectively). Equations 3 and 4, on the other hand, evidence a scarcely noticeable shrinkage on transferring 1 mol of acid from the pure state to dilute sulfolane solutions. This supplies evidence for the supposition of only negligible interactions between like and unlike molecules. As previously pointed out (*14*) the steric hindrance of the globular sulfolane molecule prevents the exposed negative end of its dipole from interacting with cations even if of reduced dimensions, as protons are; the very low autoprotolysis constant (p$k \simeq 25$) as well as the Walden products of alkali halides (*15*), unusually high for a nonaqueous solvent, account for this supposition. In the case of pure alkanoic acids a COOH group contribution of 23.65 may be derived from our experimental volume data, taking into account the contribution of the aliphatic section of the acid molecule. (A value of 34.33 indeed may be ascribed, to first approximation, to the CH_3 group on extrapolation, at $n(CH_2) = 0$, of C_5–C_{10} liquid alkane volumes measured at 303.16 K.) With the same procedure a value of ~21 may be calculated, at 298.16 K, from volumes of C_4–C_8 alkanedioic acids (*16*); the agreement between the two values may be judged satisfactory taking into account the heterogeneity of the material reported in the literature.

A more complete picture of the behavior of n-alkanoic acids implies the calculation of the void volumes of molecules, which should be responsible for interactions of any kind. Therefore, we calculated the van der Waals volumes by means of the equation

$$v_w = \frac{V°_{298.16K}}{1 + \Delta H_v^{T_B}/\Delta H_v^{298.16K}} \qquad (6)$$

which was already (*1*) illustrated (the symbols in eq 6 have the usual meanings and ΔH_v^T are the vaporization enthalpies at the temperature T). Table VIII summarizes the properties needed to calculate v_w; vaporization enthalpies are taken from the calorimetric measurements of Cox and Pilcher (*17*). Two sets of $\Delta H_v^{T_B}$ are reported in Table VIII. The first set (a) refers to experimental data reported by Riddick and Bunger (*18*); a Trouton rule type equation

$$\Delta H_v^{T_B} = 23.0T_B \qquad (7)$$

reproduces these data reasonably well (column b in Table VIII), the exception being acetic acid; in the case of the last term experimental data are lacking. The second set of data (c), which are, on the other hand, in very good agreement with the first set, are calculated by an emprical formula suggested by Moshino et al. (*19*), who successfully predict vaporization enthalpies, at T_B, from refractive index measurements at 298.16 K. The validity of their formula was tested by using thermal data for ~500 substances. The so calculated v_w values exhibit a linear deendence on the number of CH_2 groups in the acid molecule:

$$v_w = 33.77 + 10.62n(CH_2) \qquad (8)$$

Then from eq 3, 4, and 8, correlating the volumes $V°$, $\bar{v}_2$, and v_w to the number of CH_2 groups in the n-alkanoic acid molecules, eq 3′ and 4′ were derived, which correlate the volumes

$$V° = 3.290 + 1.620v_w \qquad (3')$$

$$\bar{v}_2 = 3.267 + 1.582v_w \qquad (4')$$

$V°$ and $\bar{v}_2$ to van der Waals volumes. The van der Waals volumes in eq 3′ and 4′ appear multiplied by a factor (~1.6) larger than unity, as previously (*2*) observed for several series of organic substances (n-alkanes, primary alcohols, diols, nitriles, ammines). This numerical factor does not change by introducing into the molecule different functional groups; this may be interpreted in terms of an impenetrable molar volume larger than v_w, in a constant extent, because of some intrinsic geometrical factors; hence, the volume $V - 1.6v_w$ may be equated to the void volume, which should be modified by interactions. This void volume should be ~3.3 $cm^3 \cdot mol^{-1}$ in the case of *n*-alkanoic acids, as calculated from our measurements, both in the pure state and in sulfolane solutions.

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Registry No. Sulfolane, 126-33-0; acetic acid, 64-19-7; propionic acid, 79-09-4; butyric acid, 107-92-6; valeric acid, 109-52-4; caproic acid, 142-62-1.

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Isobaric Vapor–Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane. The System 1,3-Dioxolane–Chlorobenzene

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The isobaric vapor–liquid equilibria of the system 1,3-dioxolane–chlorobenzene was studied with a Stage–Muller apparatus at pressures P = 300, 500, 650, 740 mmHg. The P-t-x-y data were analyzed by means of the Wilson expressions and show a poor thermodynamic consistency when checked with the area test, accounting for the deviation of the vapor phase from the ideal gas behavior and neglecting the contribution of the small values of the heat of mixing. A better consistency is obtained if association between the components is assumed.

Introduction

This paper pursues our systematic research on vapor–liquid (VLE) measurements of the binary systems containing 1,3-dioxolane, with the aim of comparing the thermodynamic properties of a set of binary mixtures having one component unchanged and the other chosen with varying functional groups. We shall focus our attention on the correlability of the VLE data by means of the same expression (we have considered the Wilson relationship to be particularly important), on the possible trend of the energy parameters in the correlation equation, on the volatility of components, etc. (*1–6*). Since some VLE data have shown unsatisfactory thermodynamic consistency (area test), we have set up an LKB flow microcalorimeter to obtain heat of mixing data that are necessary to have the enthalpy term in the Gibbs–Duhem equation. The mixture 1,3-dioxolane–chlorobenzene studied in this paper, though revealing small values of the heat of mixing (*7*) and therefore the best conditions for application of the area test, has shown a complicated interaction pattern of the molecules which is referred to in the Conclusions.

Experimental Section

Chemicals Used. The 1,3-dioxolane (Fluka product, analytical grade, 99%) was purified following the procedure given in ref 1. Chlorobenzene was C. Erba (Milan, Italy) RPE product; purity 99.5%. The major impurity, water 0.1%, was removed by drying with molecular sieve 3A followed by distillation.

The refractive index of purified 1,3-dioxolane is n^{25}_D = 1.3990: the literature values are n^{20}_D = 1.3974 (*8*) and n^{20}_D = 1.4000 (*9*). For purified chlorobenzene we have n^{25}_D = 1.5219 and n^{20}_D = 1.5245, whereas the literature value is n^{20}_D = 1.5241 (*8*).

1,3-Dioxolane (dioxolane) is component 1.

VLE Measurements

The isobaric VLE data P-t-x-y were obtained at pressures P = 300, 500, 650, 740 mmHg, with a Stage–Muller apparatus described in ref 10 (Figure 1). For further details on the equipment see also ref 11.

The equilibrium temperature was measured by a standard mercury-in-glass thermometer having an accuracy of ±0.1 °C.

The pressure was measured with a mercury filled U-tube manometer. The maximum error in the pressure measurement

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