Glossary

ϵ^E	excess dielectric constant
η^E	excess viscosity
P^E	excess molar polarization
x	mole fraction of the toluene
d	density

Registry No. Acetonitrile, 75-05-8; toluene, 108-88-3.

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Infinite-Dilution Activity Coefficients from Ebulliometric Isobaric Bubble Point–Composition Data of Hydrocarbon–Sulfolane Systems

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Isobaric bubble point temperature vs. composition data have been measured for three partially miscible binaries of hydrocarbon and sulfolane in their respective miscible regions at three different pressures. The limiting slopes, $(\partial T/\partial x)_P^\infty$ values, have been obtained in the sulfolane-dilute and hydrocarbon-dilute regions from the regression analysis of the experimental data for straight line relations. The activity coefficients at infinite dilution have been calculated at varied temperatures at two widely different temperature levels. These values can be used as a data source for evaluation of the group-interaction parameters for CH_2–sulfolane pair of groups and their temperature dependency in the modified UNIFAC/SUPERFAC model.

Introduction

Liquid–liquid extraction (LLE) of aromatic hydrocarbons from petroleum fractions is of great commercial importance and is carried out by using a selective polar solvent such as sulfolane. The liquid–liquid equilibrium data needed for the process engineering calculations are conveniently predicted by using the modified UNIFAC group-interaction model (1, 2) as only five groups are involved such as (1) ACH, (2) ACCH₃, (3) CH₂, (4) CH₃, and (5) sulfolane. Since CH₃ and CH₂ are classified under the same main group, there are in all six possible pairs of groups and only six group-interaction parameters are needed for the prediction of LLE data (3, 4). The activity coefficients at infinite dilution are considered an excellent data source for evaluation of the group-interaction parameters, especially for the CH₂–sulfolane pair of groups, as they are obtained from the binaries which are miscible only in the very dilute regions. Besides they can be determined by a relatively simple differential ebulliometric technique with reliable accuracy. This technique requires less experimental time and is well suited for the binaries whose boiling points differ widely. In the present work the activity coefficients at infinite dilution have been de-

termined from the isobaric bubble point temperature vs. composition data in the respective miscible regions of three partially miscible binaries: (i) n-hexane–sulfolane, (ii) n-heptane–sulfolane, and (iii) cyclohexane–sulfolane. The physical properties of the pure components (5, 6) are presented in Table I and the solubility limits of the three partially miscible binaries (7, 8) in Table II.

Thermodynamic Relations

Gautreaux and Coates (9) developed an expression for activity coefficients at infinite dilution in terms of pure component properties and the limiting slope of the temperature with respect to the liquid phase mole fraction, which was further improved by Null (10) by including vapor–phase nonidealities as

$$\gamma_{1,\text{exptl}}^\infty = [P_2^S - [1 - (P_2^S v_2^L/RT) + (P_2^S/\phi_2^S) \times \\ (\partial\phi_2^S/\partial P)_T](dP_2^S/dT)(\partial T/\partial X_1)_P^\infty]/[(P_1^S\phi_1^S/\phi_{1,P_2}s) \times \\ \exp[(P_2^S - P_1^S)v_1^L/RT]] \quad (1)$$

where the pure component vapor pressures, P_i^S, and liquid molar volumes, v_i^L, are readily available in the literature (5, 6) as a function of temperature. The fugacity coefficients of the pure components at the saturated vapor pressures, ϕ_i^S, their derivatives with respect to pressure $(\partial\phi_i^S/\partial P)_T$, and the fugacity coefficient of component i evaluated at P_j^S, $\phi_{i,P_j}s$, have been determined by using the virial equation of state with the second virial coefficients estimated by the method of Tsonopoulos (11, 12). The limiting slope of temperature with respect to liquid-phase composition, $(\partial T/\partial X)_P^\infty$, is only required to be obtained experimentally by the differential ebulliometric technique. However, due to experimental difficulties in directly measuring the liquid-phase compositions, x, in equilibrium with the vapor phase in the ebulliometer, this limiting slope has been calculated in terms of $(\partial T/\partial X_F)_P^\infty$, where x_F is the composition of the dilute mixture feed charged to the ebulliometer. It can be seen (13) that the two limiting slopes are related as

$$(\partial X_1/\partial T)_P^\infty = (\partial X_F/\partial T)_P^\infty + L_2\theta/RT^2 \quad (2)$$

where L_2 is the latent heat of vaporization of component 2 and θ the fraction of the feed that is present in the vapor phase, which can be easily estimated from the free vapor space of the

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Table I. Properties of Pure Components (5, 6)

property	n-hexane	n-heptane	cyclohexane	sulfolane
normal bp, K	341.9	371.6	353.9	558.1
critical const				
P_c, atm	29.3	27.0	40.2	56.2[a]
V_c, cm^3/(g mol)	370.0	432.0	308.0	314.7[a]
T_c, K	507.4	540.2	533.4	840.8[a]
Z_c	0.264	0.263	0.273	0.257[a]
acentric factor, ω	0.2957	0.3507	0.2144	0.4470[a]
const in Antoine eq[b]				
A	15.8366	15.8737	15.7527	22.7681
B	2697.55	2911.32	2766.63	11120.91
C, K	−48.78	−56.51	−50.50	133.04
liq molar vol const[c]				
a, cm^3/(g mol)	125.959	125.800	92.915	83.234
$10^2 b$, cm^3/(g mol)	−14.4560	−6.0278	−2.4860	1.7531
$10^4 c$, cm^3/(g mol)	5.472	4.116	2.616	0.732

[a] Estimated by the method of Hakuta and Hirata (17). [b] $\ln P = A - B/(T + C)$, where P is in mmHg and T in K. [c] $V^L = a + bT + cT^2$ (from ref 7).

Table II. Mutual Solubility Data for the Three Partially Miscible Systems at 303.1 K (7, 8)

	phase 1		phase 2	
system	x_{21}	x_{11}	x_{12}	x_{22}
sulfolane (1)–cyclohexane (2)	0.0385	0.9615	0.0026	0.9974
sulfolane (1)–n-hexane (2)	0.0339	0.9661	0.0023	0.9977
sulfolane (1)–n-heptane (2)	0.0207	0.9793	0.0021	0.9979

ebulliometers, which is about 100 cm^3 for all the ebulliometers whereas the liquid sample taken is 50 cm^3. The limiting slope, $(\partial T/\partial X_F)_P^\infty$ has been obtained by statistical regression analysis for correlating the experimental $(\Delta T - x_F)$ data in the dilute regions to a straight-line relation (14) expressed as

$$\Delta T = a x_F \qquad (3)$$

where ΔT is the difference in the boiling points of the pure component and the mixture.

Experimental Section

The isobaric $(T - x_F)$ data have been determined at three different pressures of 600, 700, and 750 mmHg by using the experimental setup as described in Figure 1. The details of the experimental procedure are available elsewhere (13). The temperatures have been measured in the sulfolane-dilute region by a 0–200 °C range digital temperature indicator with Pt-100 sensor with an accuracy better than ±0.05 °C and in the sulfolane-rich region with a digital millivoltmeter with an accuracy in temperature measurement better than ±0.25 °C. It may be noted that the bubble point temperatures of all dilute mixtures in the sulfolane-rich region range between 208 and 280 °C and due to the comparatively large temperature gradients it is difficult to maintain the temperature constant even when the pressure is maintained constant. However, the experimental run at a particular pressure has been repeated twice and has been found to be reproducible within ±1 °C. The average value has been taken for the equilibrium temperature. Considering the large temperature gradients at the sulfolane-rich region, the fluctuations in temperature of this order of magnitude may be considered insignificant. Further, it is reported in the literature (15) that sulfolane exhibits good thermal stability up to a temperature of 220 °C. Above this temperature it slowly produces SO$_2$ and unsaturated, probably polymeric, material which imparts brownish color to the liquid. However, it decomposes at a very slow rate (of the order of 0.02 mol %/h at 240 °C) and the major cause of degradation is the influence of oxygen. Boiling point measurements of pure sulfolane after prolonged heating under the present experimental condition having nitrogen atmosphere have showed very little loss of purity although considerable discoloration has been observed.
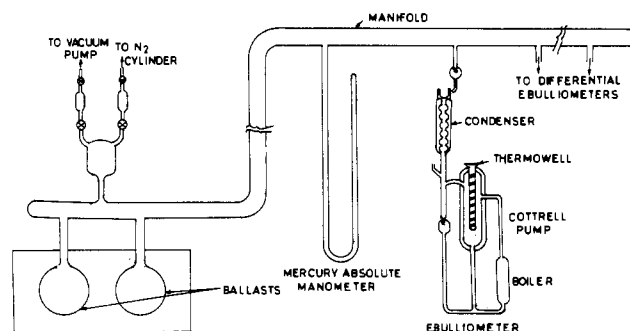

Figure 1. Experimental setup.

In the case of mixtures as well, the change in color has been observed at the end of each experimental run (equilibrium could be obtained within 1 h). But since every time fresh sulfolane has been used, it can be confidently mentioned that the very small degradation of sulfolane above 240 °C has not affected our measurements to any significant extent.

The compositions of the feed solutions were prepared with accuracy better than ±0.0001 mol % in the sulfolane-rich region and ±0.0005 mol % in the hydrocarbon-rich region. The pressures have been maintained constant and measured by an absolute mercury manometer with an accuracy better than ±1 mmHg. All pure components used were AnalaR grade chemicals having 99.99% purity. The boiling points of the pure substances have been found to agree with the reported values (Table I) within the experimental uncertainties in temperature measurements.

Results and Discussion

The bubble point temperature vs. feed composition data for the three binaries cyclohexane–sulfolane, n-heptane–sulfolane, and n-hexane–sulfolane in their respective miscible regions at three pressures 600, 700, and 750 mmHg are presented in Tables V–X and plotted in Figures 2–7. From regression analysis of these data for straight-line relations, it is observed that the standard deviations of the $(\Delta T - x_F)$ data in the sulfolane-dilute and hydrocarbon-dilute regions are very small and are of the order of magnitude 10^{-1} °C. The limiting slopes for the three binaries are presented in Table III and their accuracies range in the order of magnitude between 10^{-3} and 10^{-2}. The activity coefficients at infinite dilution, $\gamma_{i,\text{exptl}}^\infty$ have been calculated by using eq 1 at each temperature from the isobaric limiting slopes values $(\partial T/\partial x)_P^\infty$ and are presented in Table IV. As can be expected γ^∞ values for all components decrease with increasing temperature and γ^∞ values of polar sulfolane are of larger magnitude than those for nonpolar hydrocarbons. It should be noted that since the bubble point temperature vs.

Table III. Limiting Slopes at Different Temperatures

			sulfolane-dilute end			hydrocarbon-dilute end	
system	press., mmHg	T, K	$(\partial T/\partial x_F)_P^\infty$	$(\partial T/\partial x)_P^\infty$	T, K	$(\partial T/\partial x_F)_P^\infty$	$(\partial T/\partial x)_P^\infty$
sulfolane–cyclohexane	600	347.6	−1183.8	−1541.6	546.2	−3840.4	−5885.4
	700	352.6	−1061.9	−1383.9	552.7	−3290.1	−4948.9
	750	354.6	−958.1	−1230.2	555.6	−2911.8	−4237.7
sulfolane–n-heptane	600	363.3	−625.5	−738.3	546.2	−3572.2	−5278.0
	700	368.1	−488.1	−552.3	552.5	−3043.7	−4413.9
	750	370.5	−423.1	−469.8	555.5	−2712.5	−3829.2
sulfolane–n-hexane	600	334.6	−2341.2	−5535.8	546.3	−3957.2	−6162.4
	700	339.2	−2195.0	−4857.4	552.7	−3541.0	−5539.2
	750	341.4	−1922.1	−3793.1	555.6	−3281.1	−5067.8
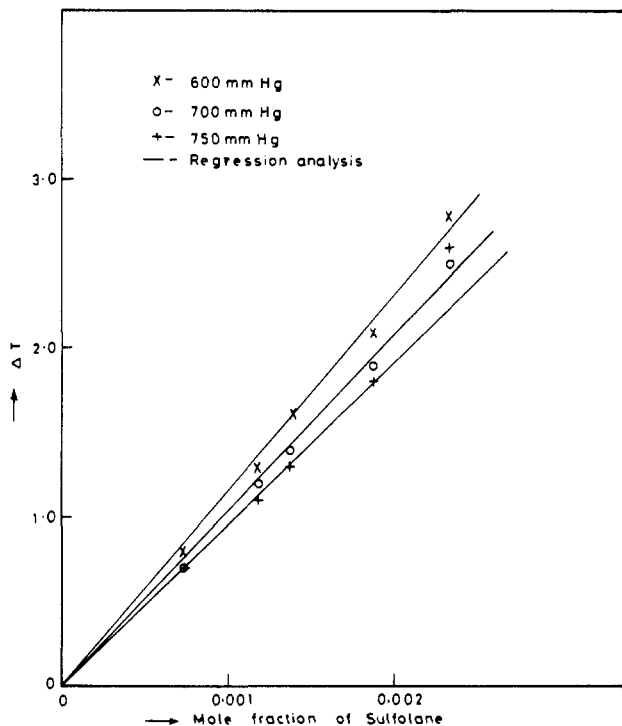
Figure 2. ΔT–x_F diagram for the n-hexane–sulfolane system (sulfolane-dilute end).
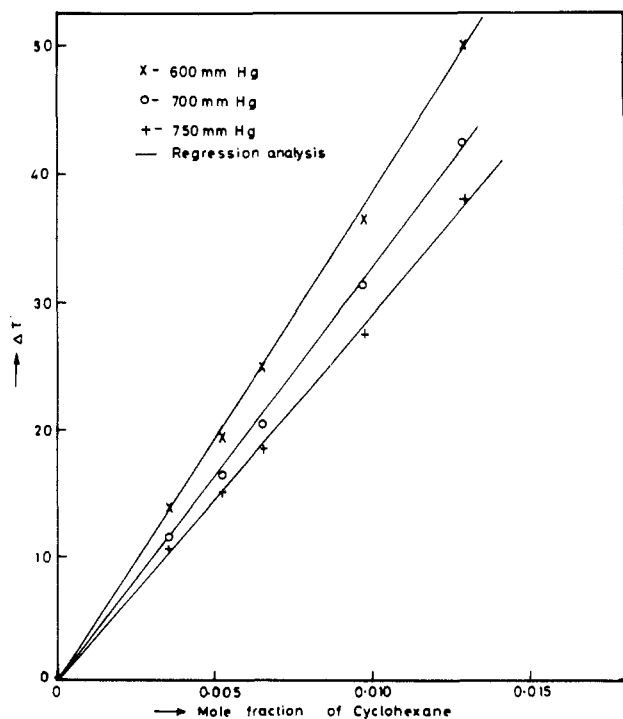
Figure 3. ΔT–x_F diagram for the n-hexane–sulfolane system (sulfolane-rich end).

Table IV. γ^∞ vs. Temperature Data for the Systems Sulfolane–Cyclohexane, Sulfolane-n-Heptane, and Sulfolane-n-Hexane

system	temp, K	γ_1^∞	temp, K	γ_2^∞
sulfolane (1)–cyclohexane (2)	347.6	129.90	546.2	4.768
	352.6	98.87	552.7	4.329
	354.6	90.00	555.6	3.842
sulfolane (1)–heptane (2)	363.3	120.68	546.2	5.615
	368.1	108.30	552.5	5.114
	370.5	102.84	555.5	4.592
sulfolane (1)–hexane (2)	334.6	139.85	546.3	4.693
	339.2	121.43	552.7	4.609
	341.4	110.58	555.6	4.390

Table V. ΔT–x_F Data for Sulfolane-n-Hexane System in the Sulfolane (1)-Dilute Region

	600 mmHg		700 mmHg		750 mmHg	
x_1	t, °C	Δt, °C	t, °C	Δt, °C	t, °C	Δt, °C
0.000 00	61.5	0.0	66.1	0.0	68.3	0.0
0.001 00	59.8	1.7	64.0	2.1	66.1	2.2
0.001 90	57.8	3.7	62.0	4.1	64.0	4.3
0.002 10	57.7	3.8	61.8	4.3	63.8	4.5
0.002 95	56.0	5.5	59.6	6.5	61.3	7.0
0.003 85	54.2	7.3	57.8	8.3	59.5	8.8

Table VI. ΔT–x_F Data for Sulfolane-n-Hexane System in the n-Hexane (1)-Dilute Region

	600 mmHg		700 mmHg		750 mmHg	
x_1	t, °C	Δt, °C	t, °C	Δt, °C	t, °C	Δt, °C
0.000 00	273.2	0.0	279.6	0.0	282.5	0.0
0.001 24	268.3	4.9	275.1	4.5	278.5	4.0
0.002 75	262.1	11.1	269.8	9.8	273.3	9.2
0.007 62	243.3	29.9	252.6	27.0	257.7	24.8
0.010 69	230.8	42.4	242.0	37.6	247.5	35.0
0.013 57	219.5	53.7	231.7	47.9	237.6	44.6

Table VII. ΔT–x_F Data for the Sulfolane-n-Heptane System in Sulfolane (1)-Dilute Region

	600 mmHg		700 mmHg		750 mmHg	
x_1	t, °C	Δt, °C	t, °C	Δt, °C	t, °C	Δt, °C
0.000 00	90.2	0.0	95.0	0.0	97.4	0.0
0.000 75	89.7	0.5	94.6	0.4	97.1	0.3
0.001 64	89.2	1.0	94.2	0.8	96.7	0.7
0.001 90	89.0	1.2	94.1	0.9	96.6	0.8
0.002 40	88.7	1.5	93.8	1.2	96.4	1.0
0.002 65	88.5	1.7	93.7	1.3	96.3	1.1
0.003 05	88.3	1.9	93.5	1.5	96.1	1.3

Table VIII. ΔT–x_F Data for the Sulfolane-n-Heptane System in the n-Heptane (1)-Dilute Region

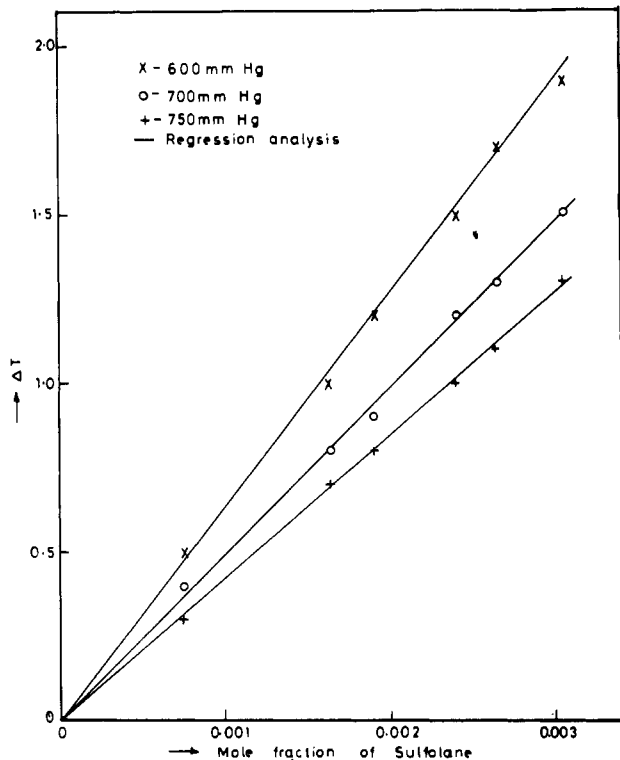|	600 mmHg		700 mmHg		750 mmHg	
x_1	t, °C	Δt, °C	t, °C	Δt, °C	t, °C	Δt, °C
0.000 00	273.1	0.0	279.4	0.0	282.4	0.0
0.001 78	266.8	6.3	274.1	5.3	277.4	5.0
0.003 90	259.1	14.0	267.5	11.9	271.6	10.8
0.008 70	241.8	31.3	253.0	26.4	258.9	23.5
0.014 20	223.0	50.1	236.0	43.4	244.0	38.4
0.018 27	207.9	65.2	223.8	55.6	232.8	49.6

Figure 4. ΔT-x_F diagram for the n-heptane–sulfolane system (sulfolane-dilute end).

Figure 6. ΔT-x_F diagram for the cyclohexane–sulfolane system (sulfolane-dilute end).
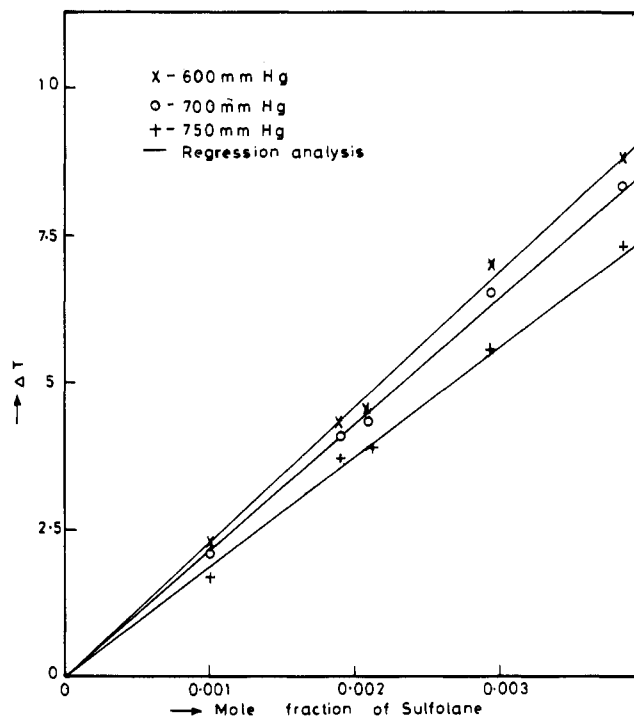

Figure 5. ΔT-x_F diagram for the n-heptane–sulfolane system (sulfolane-rich end).
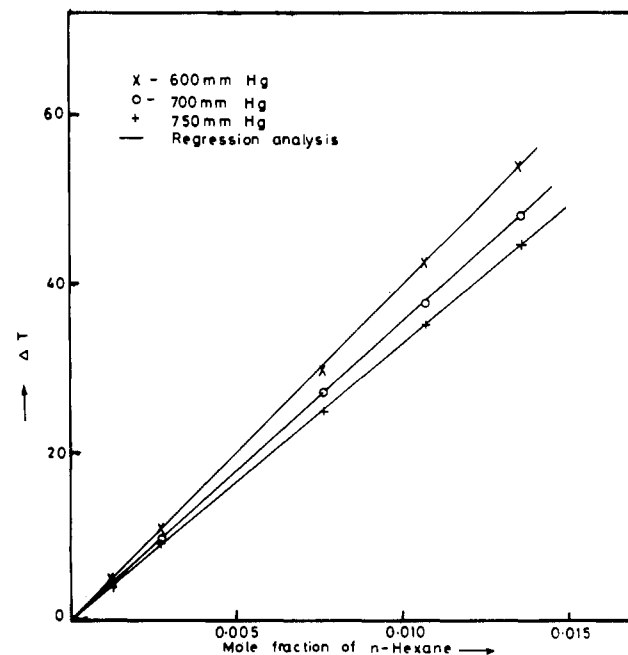

Figure 7. ΔT-x_F diagram for the cyclohexane–sulfolane system (sulfolane-rich end).

Table IX. ΔT-x_F Data for the Sulfolane–Cyclohexane System in the Sulfolane (1)-Dilute Region

	600 mmHg		700 mmHg		750 mmHg	
x_1	t, °C	Δt, °C	t, °C	Δt, °C	t, °C	Δt, °C
0.000 00	74.5	0.0	79.5	0.0	81.5	0.0
0.000 73	73.7	0.8	78.8	0.7	80.8	0.7
0.001 18	73.2	1.3	78.3	1.2	80.4	1.1
0.001 37	72.9	1.6	78.1	1.4	80.2	1.3
0.001 89	72.4	2.1	77.6	1.9	79.7	1.8
0.002 34	71.7	2.8	77.0	2.5	78.9	2.6

Table X. ΔT-x_F Data for the Sulfolane–Cyclohexane System in the Cyclohexane (1)-Dilute Region

	600 mmHg		700 mmHg		750 mmHg	
x_1	t, °C	Δt, °C	t, °C	Δt, °C	t, °C	Δt, °C
0.000 00	273.1	0.0	279.6	0.0	282.5	0.0
0.003 50	259.1	14.0	268.1	11.5	272.0	10.5
0.005 22	253.6	19.5	263.1	16.5	267.6	15.0
0.006 50	248.1	25.0	258.1	20.5	264.0	18.5
0.009 70	236.6	36.5	248.1	31.5	255.0	27.5
0.012 88	223.1	50.0	237.1	42.5	244.5	38.0

composition data are employed at isobaric condition, the γ^∞ values for sulfolane and hydrocarbons in Table IV are at widely different temperature levels. However, the temperature de-

pendency of these limiting activity coefficients at different temperature levels can be conveniently incorporated in order to evaluate the temperature dependency of the group-interaction parameters by the SUPERFAC model for the activity coefficient (16).

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Excess Molar Volumes of 1-Alkanol (C₁–C₅) Binary Mixtures with Acetonitrile

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Excess molar volumes (V^E) for binary mixtures containing acetonitrile and a 1-alkanol (C₁–C₅) measured dilatometrically at 308.15 K are reported over the entire range of compositions. Equimolar excess volumes increase linearly with increase in the number of carbon atoms in the hydrocarbon chain. The V^E–x curve is skewed toward low acetonitrile mole fraction for ethanol to 1-pentanol. The results are rationalized in terms of the physical and specific interactions in these mixtures.

Introduction

Acetonitrile, 1-alkanols (C₁–C₅), and their binary mixtures are frequently used as solvents in chemistry and modern technology (1, 2). We report here the excess molar volumes for methanol (MeOH) + acetonitrile (AN), ethanol (EtOH) + AN, 1-propanol (PrOH) + AN, 1-butanol (BuOH) + AN, and 1-pentanol (AmOH) + AN mixtures at 308.15 K and over the whole mole fraction range measured by using a continuous dilution dilatometer.

Experimental Section

Benzene (B.D.H., AnalaR), cyclohexane (Glaxo, L.R.), acetonitrile (E. Merck), methanol (B.D.H., AnalaR), ethanol (Bengal Chemicals, dehydrated), and 1-propanol (Riedel) were purified by recommended methods (3, 4). Purity of the solvents was ascertained by the constancy of their boiling temperatures during final distillations and also by comparing their densities, determined by a pycnometric technique with the corresponding literature values (Table I). Mercury needed for calibrations and used for use in the dilatometer was purified first by washing several times with 5% nitric acid and then with water till free from acid. It was then dried and distilled under partial vacuum. Due to its contact with the liquids in the dilatometer, mercury required purification afterone complete experiment.

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Table I. Densities of Pure Liquids at 308.15 K

	ρ, g cm⁻³	
component	this study	lit. (3, 4)
acetonitrile	0.7656	0.7659
benzene	0.8629	0.8630
1-butanol	0.7982	0.7987
cyclohexane	0.7644	0.7644
ethanol	0.7766	0.7768
methanol	0.7772	0.7770
1-pentanol	0.8039	0.8041
1-propanol	0.7918	0.7916

A continuous dilution dilatometer was used for volume measurements (5). Temperature of the measurements was controlled to within ±0.01 K. The procedural details of the method are practically the same as described by earlier workers. The mole fractions and the excess volumes are believed to be precise to within ±0.0002 and ±0.005 cm³ mol⁻¹, respectively. Working of the dilatometer was checked by measuring V^E of benzene + cyclohexane mixtures as recommended by the previous workers (6, 7). Our equimolar V^E value at 298.15 K was 0.644 cm³ mol⁻¹ as compared to the literature (7) value of 0.6496 cm³ mol⁻¹. The deviations from the corresponding literature values at other mole fractions were within ±0.01 cm³ mol⁻¹.

Results and Discussion

The V^E values for MeOH + AN, EtOH + AN, PrOH + AN, BuOH + AN, and AmOH + AN at 308.15 K and over the whole mole fraction range are given in Table II. The composition dependence of V^E was correlated by the polynomial (1)

$$V^E/(\text{cm}^3 \text{ mol}^{-1}) = x(1-x)\sum_{i=0}^{R} v_i(2x-1)^i \qquad (1)$$

where x is the mole fraction of acetonitrile. The estimates of the parameters v_i were obtained by the method of least squares and are collected in Table III. The deviations δV^E of the experimental values from the calculated (least squares) ones