

- Proc. R. Soc. London, Ser. A*, **240**, 1 (1957).
- (11) Haselden, G. G., Newitt, D. M., Shah, S. M., *Proc. R. Soc. London, Ser. A*, **209**, 1 (1951).
- (12) Khazanova, N. E., Lesnevskaja, L. C., Saxarova, A. V., *Khim. Promst. (Moscow)*, **44**, 364 (1966).
- (13) Kuenen, J. P., *Philos. Mag. Suppl.*, **5**, 44, 174 (1897); Kuenen, J. P., Tobson, W. G., *Philos. Mag.*, **4**, 116 (1902).
- (14) Mollerup, J., *J. Chem. Soc., Faraday Trans. 1*, in press.
- (15) Nagahama, K., Konishi, H., Hoshino, D., Hirata, M., *J. Chem. Eng. Jpn.*, **7**, 323 (1974).
- (16) NGPA Research Report 5, Tulsa, Okla., 1971.

- (17) Prausnitz, J. M., Chueh, P. L., "Computer Calculations for High-Pressure Vapor-Liquid Equilibria", Prentice-Hall, New York, N.Y., 1968.
- (18) Rowlinson, J. S., Sutton, J. R., Weston, J. F., *Proc. Jt. Conf. Thermodyn. Transp. Prop. Fluids*, Inst. Mech. Engr.
- (19) Van Ness, H. C., Beyer, S. M., Gibbs, R. E., *AIChE J.*, **19**, 238 (1973).

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The Density and Enthalpy of Mixing of Solutions of Acetonitrile and of Dimethyl Sulfoxide with Several Aromatic Hydrocarbons

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The density at 30.0 °C was measured for solutions of acetonitrile and of dimethyl sulfoxide with benzene, 1,4-dimethylbenzene, and 1,3,5-trimethylbenzene. The excess enthalpy of mixing was measured by flow microcalorimetry at 25.0 °C for the same systems plus solutions with 1,2,4-trimethylbenzene. All of the enthalpies of mixing are endothermic. With both acetonitrile and dimethyl sulfoxide the enthalpies of mixing at one-half mole fraction become more positive in the order benzene < 1,4-dimethylbenzene < 1,2,4-trimethylbenzene < 1,3,5-trimethylbenzene. Excess volumes were calculated from the solution densities. The excess volumes are negative in the benzene solutions, but they are positive for the 1,3,5-trimethylbenzene solutions. The trends in excess enthalpy and excess volume are consistent with the observed liquid-liquid immiscibility below 21.6 °C in 1,3,5-trimethylbenzene-dimethyl sulfoxide solutions.

This paper is part of a continuing series of a study of the properties of binary mixtures of aromatic hydrocarbons with polar molecules. Previous reports have been made on hydrocarbon-nitroalkane mixtures (6, 7, 8, 12). The present paper reports the density at 30 °C and the enthalpy of mixing at 25

°C of aromatic hydrocarbon solutions of acetonitrile and of dimethyl sulfoxide. Several of these solutions have been studied by others. There are reports of the density, excess volume, excess Gibbs energy, and enthalpy of mixing of benzene-acetonitrile mixtures (3, 4, 5) and of excess volume, enthalpy of mixing, and excess Gibbs energy of mixing of benzene-dimethyl sulfoxide mixtures (1, 9, 16, 18).

Experimental Section

Solution Components. Summarized in Table I are the source, purification, density, and refractive index of the solution component compounds acetonitrile, dimethyl sulfoxide, benzene, 1,4-dimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene. The method of acetonitrile purification was that of O'Donnell, Ayres, and Mann (22). The physical properties agree satisfactorily with accepted literature values.

Experimental Methods. Density. Densities were determined in a 16-cm³ density bottle with a constant bore capillary neck of (1.00 ± 0.08) mm which was graduated in 1-mm intervals for a length of 2 cm. The bottle was calibrated with freshly boiled distilled water. The density measurements were made at (30.00 ± 0.01) °C.

Solutions for the measurement of density were prepared

Table I. Source, Purification, and Physical Properties of Solution Components

Compound	Source	Purification	Bp, °C (mmHg)	d_{30} , g cm ⁻³	n_{25}^D
Acetonitrile	Fisher certified 99 mol %	Refluxed with Na ₂ CO ₃ and KMnO ₄ , distilled, acidified, filtered, distilled thru 24-in. helice packed column	80 (742)	0.77145	1.34140
Dimethyl sulfoxide	Fisher certified ACS grade	Dried over 4A molecular sieve, fractionally crystallized, distilled from CaH ₂ thru 24-in. helice packed column	80 (20)	1.0913	1.4770 (20°)
Benzene	Phillips pure grade, 99 mol %	Shaken with successive portion of H ₂ SO ₄ , water washed until neutral to litmus, dried over CaSO ₄ , distilled from CaH ₂ thru 24-in. helice packed column	79.3 (742)	0.86838	1.49800
1,4-Dimethylbenzene (<i>p</i> -xylene)	Eastman practical grade	Dried over CaSO ₄ , distilled from CaH ₂ thru 24-in. helice packed column	137.5 (742)	0.85230	1.49320
1,2,4-Trimethylbenzene (pseudocumene)	Phillips research grade	Lot no. 1345, 99.89 mol %, used without purification		0.86796	1.50250
1,3,5-Trimethylbenzene (mesitylene)	Eastman practical grade	Dried over CaSO ₄ , distilled from sodium thru 24-in. helice packed column	162.5 (740)	0.85572	1.49610

Table II. Density and Mole Fraction of the Acetonitrile and Dimethyl Sulfoxide-Hydrocarbon Solutions (g cm⁻³, 30.0 °C)

X_2	d	X_2	d	X_2	d
Benzene (1)-acetonitrile (2)		1,4-Dimethylbenzene (1)-acetonitrile (2)		1,3,5-Trimethylbenzene (1)-acetonitrile (2)	
0.1650	0.8588	0.1425	0.8474	0.1540	0.8502
0.2431	0.8535	0.3179	0.8398	0.2367	0.8462
0.3032	0.8496	0.5054	0.8289	0.3989	0.8301
0.3670	0.8444	0.6144	0.8202	0.5478	0.8278
0.4253	0.8394	0.7031	0.8122	0.6018	0.8236
0.4822	0.8339	0.7776	0.8037	0.6482	0.8197
0.5223	0.8307	0.8391	0.7964	0.6917	0.8151
0.5816	0.8242	0.8976	0.7877	0.7275	0.8113
0.6243	0.8198	0.9434	0.7808	0.7673	0.8074
0.7100	0.8100			0.8037	0.8024
0.7926	0.8003			0.8590	0.7947
0.8686	0.7898			0.9115	0.7809
0.9301	0.7809			0.9580	0.7786
Benzene (1)-dimethyl sulfoxide (2)		1,4-Dimethylbenzene (1)-dimethyl sulfoxide (2)		1,3,5-Trimethylbenzene (1)-dimethyl sulfoxide (2)	
0.1430	0.8967	0.1888	0.8812	0.2157	0.8836
0.2500	0.9181	0.3189	0.9040	0.3500	0.9050
0.3526	0.9393	0.4294	0.9585	0.4651	0.9260
0.4562	0.9609	0.5355	0.9487	0.5187	0.9373
0.5447	0.9803	0.5815	0.9596	0.5679	0.9482
0.6452	1.0029	0.6204	0.9703	0.6584	0.9702
0.7241	1.0217	0.6305	0.9718	0.7368	0.9918
0.8180	1.0439	0.6743	0.9833	0.8064	1.0137
0.8969	1.0632	0.7159	0.9947	0.8694	1.0354
		0.7914	1.0164	0.9321	1.0599
		0.8253	1.0278		
		0.9252	1.0616		

by weight in specially designed (2) weighing bottles with care taken to correct the mole fraction calculation for any material in the vapor phase.

Enthalpy of Mixing. The Flow Microcalorimeter. The procedure and calibration were as described before (11). The mixing chamber and thermopile, an 80-cm platinum tube of 1 mm i.d. surrounded by approximately 7500 thermocouple junctions (Beckman Instrument Co., Palo Alto, Calif.) are inside an insulated brass submarine immersed in a well-insulated water bath thermostated to $\pm 0.02^\circ$ by a remote pumping regulator. The thermopile signal is monitored by a microvolt meter (Model 150-B, Keithley Instrument Co., Cleveland, Ohio) and a strip chart recorder. Two syringe drive pumps (Harvard Apparatus Co., Millis, Mass.) fitted with gas tight syringes (Hamilton Co., Reno, Nev.) deliver the component liquids to the thermopile by way of Teflon tubing. Sixteen pumping rates ranging from 0.00137 to 0.2182 ml min⁻¹ were used. Corrections for thermal effects (20) were made, which ranged between 0.1 and 0.7% in the present work. The apparatus was calibrated using the enthalpy of neutralization of sodium hydroxide by hydrochloric acid (10, 24), and checked by determining the excess enthalpy of benzene-cyclohexane mixtures (23).

Table III. Excess Volumes. Constants for the Excess Properties Equation, Standard Deviation (30 °C, cm³ mol⁻¹)

	A_0	A_1	A_2	A_3	σ_d
Benzene (1)-acetonitrile (2)	-0.307	-0.910	—	—	0.018
1,4-Dimethylbenzene (1)-acetonitrile (2)	-0.629	-0.501	+0.371	—	0.015
1,3,5-Trimethylbenzene (1)-acetonitrile (2)	0.458	-0.218	+0.499	-0.639	0.024
Benzene (1)-Dimethyl sulfoxide (2)	-1.109	-0.663	-0.117	-0.661	0.012
1,4-Dimethylbenzene (1)-dimethyl sulfoxide (2)	-0.588	-0.403	—	—	0.009
1,3,5-Trimethylbenzene (1)-dimethyl sulfoxide (2)	0.781	-0.442	+0.953	—	0.020

Cloud Point Temperature. The 1,3,5-trimethylbenzene-dimethyl sulfoxide solutions were prepared by weight from glass syringes in 13 X 100 mm Kimax screw cap culture tubes and sealed by a cap with a Teflon faced rubber liner. The tubes were suspended in a 3-l. well-stirred water bath, and the cloud point was observed visually. Temperatures were observed on a 0.1° graduated mercury in glass thermometer which had been checked for accuracy at the ice point (6).

Results

Density and Excess Volume. The densities at 30.0 °C of solutions of acetonitrile and of dimethyl sulfoxide with benzene, 1,4-dimethylbenzene, and 1,3,5-trimethylbenzene are given in Table II at several mole fractions. The densities were converted to solution molar volumes and the excess volumes calculated from $V^E = V_{real} - V_{ideal}$. The coefficients, A_n , of the equation

$$V^E(\text{cm}^3 \text{mol}^{-1}) = x_2(1 - x_2) \sum_0^n A_n(1 - 2x_2)^n \quad (1)$$

were found by the method of least squares for the excess volume, V^E , and polar component mole fraction, x_2 . The values of the coefficients and the standard error are given in Table III. The benzene-acetonitrile values of excess volume agree satisfactorily with values in the literature (5). The benzene-dimethyl sulfoxide excess volumes are about 7% less negative at one-half mole fraction than is reported by others (1, 16, 18).

The Excess Enthalpy of Mixing. Values of the excess enthalpy of mixing, H^E , cal mol⁻¹, at various polar component mole fraction, x_2 , are given in Table IV for mixtures of acetonitrile and of dimethyl sulfoxide with benzene, 1,4-dimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene at 25.0 °C. The value of H^E at a volume fraction, $\phi = 0.5$, is marked. The coefficients of the equation

$$H^E(\text{cal mol}^{-1}) = x_2(1 - x_2) \sum_0^n A_n(1 - 2x_2)^n \quad (2)$$

were found by the method of least squares. Values of the coefficients, A_n (calories per mole), the standard error, and the maximum error are given in Table V. The value of H^E at one-half mole fraction reported here is 9.1% lower than the literature value (20) for benzene-acetonitrile. The value of H^E at half mole fraction for benzene-dimethyl sulfoxide agrees satisfactorily with two literature values. It is 0.65% more positive than one (9) and 2.1% less positive than the other (16). The equation gives the following values of the enthalpy of mixing at one-half mole fraction, $H^E_{0.5}$, the maximum enthalpy, H^E_{max} , and the polar component mole fraction of the maximum, x_2 . For acetonitrile the values of $H^E_{0.5}/H^E_{max}/x_{2max}$ are benzene 107.38/110.41/0.59, 1,4-dimethylbenzene 162.45/164.63/0.56, 1,2,4-trimethylbenzene 208.35/209.84/0.55, and 1,3,5-trimethylbenzene 233.71/235.82/0.55. For dimethyl sulfoxide the values are benzene 140.95/140.95/0.50, 1,4-dimethyl sulfoxide 254.32/255.14/0.46, 1,2,4-trimethylbenzene 282.58/282.87/0.52, and 1,3,5-trimethylbenzene partially immiscible.

Table IV. Enthalpy of Mixing, H^E (cal mol⁻¹) at Various Mole Fractions, 25 °C

X_2	H^E	X_2	H^E	X_2	H^E	X_2	H^E
Benzene (1)-acetonitrile (2)		1,4-Dimethylbenzene (1)-acetonitrile (2)		1,2,4-Trimethylbenzene (1)-acetonitrile (2)		1,3,5-Trimethylbenzene (1)-acetonitrile (2)	
0.0752	25.7	0.1022	58.0	0.1511	102.5	0.1530	119.0
0.1035	33.4	0.1480	75.8	0.4043	195.7	0.2609	171.3
0.1384	43.0	0.2383	108.6	0.4882	207.4	0.3298	198.6
0.1841	54.2	0.3037	128.7	0.5720	209.6	0.4917	233.5
0.2393	69.8	0.3789	146.3	0.6519	201.4	0.5755	235.0
0.3056	81.4	0.4607	159.0	0.7230	185.1 ^a	0.6550	225.8
0.3813	94.3	0.5447	163.6	0.7846	164.0	0.7259	208.6 ^a
0.4633	104.2	0.6254	162.1	0.8361	139.8	0.7870	185.1
0.5463	110.0	0.7011	151.4 ^a	0.9335	70.4	0.8380	156.8
0.6287	109.1 ^a	0.7674	134.3	0.9649	38.9	0.8787	128.6
0.7042	103.9	0.8225	116.2			0.9104	103.3
0.7685	93.1	0.8657	95.9			0.9344	79.9
0.8230	79.2	0.8999	76.3			0.9654	44.5
0.8664	65.4	0.9462	45.4				
0.9270	40.0						
Benzene (1)-dimethyl sulfoxide (2)		1,4-Dimethylbenzene (1)-dimethyl sulfoxide (2)		1,2,4-Trimethylbenzene (1)-dimethyl sulfoxide (2)		1,3,5-Trimethylbenzene (1)-dimethyl sulfoxide (2)	
0.1068	72.8	0.1410	158.2	0.1162	143.6	0.1568	207.5
0.1434	82.0	0.2440	218.1	0.1549	173.1	0.2678	266.7
0.1895	99.9	0.3879	249.2	0.2049	205.3	0.4178	<i>b</i>
0.2471	109.0	0.4687	255.6	0.3334	256.4	0.4999	<i>b</i>
0.3919	135.4	0.6342	239.0 ^a	0.4960	285.7	0.5830	<i>b</i>
0.4751	141.0	0.7089	214.5	0.5189	279.7	0.6626	289.0 ^a
0.5576	141.1 ^a	0.7731	186.6	0.6583	262.9 ^a	0.7340	271.6
0.6371	126.3	0.9030	100.1	0.7297	238.9	0.7944	234.2
0.7114	114.9	0.9482	63.0	0.7905	209.4	0.8431	217.0
0.8288	82.6			0.8411	172.5	0.9540	85.5
0.8709	69.6			0.8813	139.6		
0.9043	49.2			0.9532	58.0		
0.9298	38.0						

^a Enthalpy value at one-half volume fraction. ^b Mixture appeared to be partially liquid-liquid immiscible on exiting the calorimeter. Enthalpy values are 312, 310, and 310 cal mol⁻¹.

Table V. Constants for the Excess Enthalpy Equation, Standard Deviation, and Maximum Deviation (cal mol⁻¹, 25.0 °C)

Mixture	A_0	A_1	A_2	A_3	A_4	σ_d	σ_m
Benzene (1)-acetonitrile (2)	429.5	-137.8	64.4	—	—	0.60	1.5
1,4-Dimethylbenzene (1)-acetonitrile (2)	649.7	-143.9	72.4	-0.7	98.8	0.68	1.1
1,2,4-Trimethylbenzene (1)-acetonitrile (2)	833.4	-130.8	125.8	-71.4	83.9	0.27	0.4
1,3,5-Trimethylbenzene (1)-acetonitrile (2)	934.8	-165.5	139.8	-31.3	-168.8	0.65	1.0
Benzene (1)-dimethyl sulfoxide (2)	563.8	-4.4	-15.7	159.2	298.8	2.62	4.0
1,4-Dimethylbenzene (1)-dimethyl sulfoxide (2)	1017.3	91.6	391.0	66.0	—	2.21	3.9
1,2,4-Trimethylbenzene (1)-dimethyl sulfoxide (2)	1130.6	-49.6	369.3	161.8	—	1.85	3.1
1,3,5-Trimethylbenzene (1)-dimethyl sulfoxide (2) ^a	1254.2	11.3	425.0	-67.2	551.1	4.61	6.7

^a For the liquid miscible regions of 0.0-0.25 and 0.65-1.0 mole fraction dimethyl sulfoxide.

Cloud Point Temperatures. One of the solutions, 1,3,5-trimethylbenzene-dimethyl sulfoxide, forms partially miscible liquid-liquid phases below 21.6 °C. Observed values of the cloud point temperature at several mole fractions are (t_c , °C/ X_2) 21.3/0.502, 21.6/0.586, 21.4/0.587, 21.0/0.672, 20.1/0.728, and 19.5/0.802. The endothermic heat of mixing results in enough cooling, when 1,3,5-trimethylbenzene and dimethyl sulfoxide are mixed at 25.0 °C at mole ratios to give mole fractions between 0.25 and 0.65 dimethyl sulfoxide, to bring about some liquid-liquid phase separation. (See Table IV.) No liquid-liquid phase separation was observed in any of the other hydrocarbon-polar molecule solutions although some were cooled to near dry ice-acetone temperatures. The benzene-dimethyl sulfoxide system is a simple eutectic (19).

Discussion

The excess volume values are negative for benzene solutions and positive for 1,3,5-trimethylbenzene solutions of both acetonitrile and dimethyl sulfoxide. The excess enthalpy of mixing at one-half mole fraction for solutions of both polar molecules with the hydrocarbons become more positive in the order benzene < 1,4-dimethyl sulfoxide < 1,2,4-trimethylbenzene < 1,3,5-trimethylbenzene. The trends in excess volume and excess enthalpy of mixing are both consistent with the type of increasing solution complexity that leads to liquid-liquid immiscibility as is actually observed with the 1,3,5-trimethylbenzene-dimethyl sulfoxide solution. The excess Gibbs energy of benzene-acetonitrile (4) and benzene-dimethyl sulfoxide (16) solutions is positive. Our own experi-

ence with aromatic hydrocarbon-nitroalkane solutions (7, 8) leads us to predict that the excess Gibbs energy parallels the enthalpy of mixing for both acetonitrile and dimethyl sulfoxide solutions and becomes more positive in the order benzene < 1,4-dimethylbenzene < 1,2,4-trimethylbenzene < 1,3,5-trimethylbenzene.

A method of interpreting the thermodynamic properties of liquid mixtures is to treat the component molecules as an assembly of various types of segments, and to determine a single set of parameters which characterize the molecular structure and the various segment interactions. Kehiaian, Sosnowska-Kehiaian, and Hryniewicz have developed a zero-order lattice theory and applied it to obtain a set of segment surface interchange enthalpies. The surface interchange enthalpies have been successfully applied to reproduce and predict the enthalpy of mixing of aliphatic ethers with aliphatic and aromatic hydrocarbons (14) and with carbon tetrachloride (13). Kertes and Grauer (15) have extended the treatment to mixtures of amine nitrogen compounds with hydrocarbons. The enthalpy of mixing is

$$H^E = q_1 q_2 \frac{x_1 x_2}{x_1 q_1 + x_2 q_2} h^* \quad (3)$$

where q_1 is the hydrocarbon component total contact surface and q_2 is the polar molecule component (either acetonitrile or dimethyl sulfoxide) total contact surface. x_1 and x_2 are the respective mole fractions, and h^* is the molar interchange enthalpy.

The molar interchange enthalpy, h^* , contains segment interchange enthalpies of all possible segment interactions in the solution. A given segment may interact differently from molecule to molecule depending on steric, inductive, dielectric, and dispersion effects present. The present treatment cannot distinguish among these effects, but we can obtain an average segment interchange enthalpy that appears to be useful in predicting enthalpy of mixing trends in solutions containing molecules composed of these segments. In the solutions of the present study there are aliphatic segments (CH_3 —), aromatic segments (C_6H_6 , C_6H_4 —, and C_6H_3 —), and polar segments (either —CN or =SO).

The molar interchange enthalpy is given by

$$h^* = -\frac{1}{2} \sum_s \sum_t (\alpha_{1s} - \alpha_{2s})(\alpha_{1t} - \alpha_{2t}) h^*_{s,t} \quad (4)$$

where s and t represent all possible segment pair interactions, the α 's are the fraction of the total contact surface due to that segment, and $h^*_{s,t}$ is the segment molar interchange enthalpy.

The general equation for the molar interchange enthalpy when both components have aliphatic, aromatic, and polar segments is

$$h^* = -[(\alpha_{1Al} - \alpha_{2Al})(\alpha_{1Ar} - \alpha_{2Ar})h^*_{Al,Ar} + (\alpha_{1Al} - \alpha_{2Al})(\alpha_{1X} - \alpha_{2X})h^*_{Al,X} + (\alpha_{1Ar} - \alpha_{2Ar})(\alpha_{1X} - \alpha_{2X})h^*_{Ar,X}] \quad (5)$$

where $h^*_{Al,Ar}$, $h^*_{Al,X}$, and $h^*_{Ar,X}$ are the aliphatic-aromatic, aliphatic-polar, and aromatic-polar segment molar interchange enthalpies and the α 's are the fraction of the contact surface due to aliphatic (Al), aromatic (Ar), or polar (X) segments of components 1 and 2.

In the special case when benzene is mixed with a nitroalkane ($\alpha_{1Al} = \alpha_{1X} = \alpha_{2Ar} = 0$), the molar interchange enthalpy equation simplifies to

$$h^* = (1 - \alpha_{2X})h^*_{Al,Ar} - \alpha_{2X}(1 - \alpha_{2X})h^*_{Al,X} + \alpha_{2X}h^*_{Ar,X} \quad (6)$$

When the hydrocarbon component is a methyl-substituted benzene mixed with a nitroalkane ($\alpha_{1X} = \alpha_{2Ar} = 0$) the molar interchange enthalpy equation becomes

Table VI. Segment Contact Surfaces and Fractional Surfaces for Aromatic, Aliphatic, and Polar Segments

Molecule	Segment contact surface			Segment fraction of surface		
	q_{iAr}	q_{iAl}	q_{iX}	α_{iAr}	α_{iAl}	α_{iX}
C_6H_6	3.80	0	0	1.00	0	0
1,4- $\text{C}_6\text{H}_4(\text{CH}_3)_2$	3.55	1.75	0	0.67	0.33	0
1,2,4- $\text{C}_6\text{H}_3(\text{CH}_3)_3$	3.425	2.625	0	0.566	0.434	0
1,3,5- $\text{C}_6\text{H}_3(\text{CH}_3)_3$	3.425	2.625	0	0.566	0.434	0
CH_3CN A	0	0.875	1.125	0	0.438	0.562
B	0	0.875	1.625	0	0.35	0.65
$(\text{CH}_3)_2\text{SO}$	0	1.75	1.625	0	0.519	0.481

$$h^* = \alpha_{1Ar}(1 - \alpha_{2X} - \alpha_{1Al})h^*_{Al,Ar} - \alpha_{2X}(1 - \alpha_{2X} - \alpha_{1Al})h^*_{Al,X} + \alpha_{1Ar}\alpha_{2X}h^*_{Ar,X} \quad (7)$$

Kehiaian gives rules for calculating segment contact surfaces, q_i , which are based as a lattice coordination number of 8. The benzene ring contact surface was arbitrarily assigned a value based on agreement between the calculated and observed excess enthalpy values for hydrogen mixtures. Table VI gives the segment contact surfaces and contact surface fractions used in this work. Note that $\sum q_i = q$, the total molecule contact surface, and that $\sum \alpha_i = 1$ for each component molecule. We have treated the polar —CN and =SO groups as a segment. The value of 1.625 for the —CN and =SO segment contact surfaces comes from a consideration of the compounds molar volume from which a 21.5 ml mol^{-1} value was subtracted for each methyl group present in the molecule. The value of 0.875 for the — CH_3 segment contact surface comes from applying Kehiaian's rules for segment contact surface and a lattice coordination number of 8.

The experimental enthalpy of mixing at one-half mole fraction, the q and α values from Table VI, and the segment molar interchange enthalpies $h^*_{Ar,Al}$, $h^*_{Al,CN}$, and $h^*_{Al,SO}$ have been used to obtain the segment interchange enthalpies $h^*_{Ar,CN}$ and $h^*_{Ar,SO}$. We have used the $h^*_{Ar,Al}$ value of $198 \pm 7 \text{ cal mol}^{-1}$ found by Kehiaian (13, 14). A value of $h^*_{Al,SO}$ of $2900 \text{ cal mol}^{-1}$ was calculated from the infinite dilution enthalpy of dimethyl sulfoxide in *n*-hexane (17). A value of $h^*_{Al,CN}$ was calculated from the *n*-hexane-acetonitrile heat of mixing (21). Two values were tried, $h^*_{Al,CN} = 1315$ and $h^*_{Al,CN} = 1100 \text{ cal mol}^{-1}$ for $q_{\text{CH}_3\text{CN}}$ of 2.00 and 2.50, respectively. Calculated values of $h^*_{Ar,SO} = 1560 \pm 125 \text{ cal mol}^{-1}$ with $q_{(\text{CH}_3)_2\text{SO}} = 3.88$ and either $h^*_{Ar,CN} = 850 \pm 120 \text{ cal mol}^{-1}$ when $q_{\text{CH}_3\text{CN}} = 2.00$ or $h^*_{Ar,CN} = 525 \pm 50 \text{ cal mol}^{-1}$ when $q_{\text{CH}_3\text{CN}} = 2.50$ were obtained. At present we favor use of the $h^*_{Ar,CN} = 850 \pm 120 \text{ cal mol}^{-1}$ value. The segment molar interchange enthalpies and q_i values from Table VI should be of use in estimating the enthalpies of mixing of other acetonitrile and dimethyl sulfoxide hydrocarbon solutions.

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Literature Cited

- (1) Anderson, R., Cambio, R., Prausnitz, J. M., *Am. Inst. Chem. Eng. J.*, **8**, 66 (1972).
- (2) Battino, R., *J. Phys. Chem.*, **70**, 3408 (1966).
- (3) Brown, I., Fock, W., *Aust. J. Chem.*, **9**, 180 (1956).

- (4) Brown, I., Smith, F., *Aust. J. Chem.*, **8**, 62, 501 (1955).
 (5) Brown, I., Smith, F., *Aust. J. Chem.*, **10**, 423 (1957).
 (6) Clever, H. L., Pirkle, Q. R., Allen, B. J., Derrick, M. E., *J. Chem. Eng. Data*, **17**, 31 (1972).
 (7) Derrick, M. E., Clever, H. L., *J. Phys. Chem.*, **75**, 3728 (1971).
 (8) Derrick, M. E., Clever, H. L., *J. Colloid Interface Sci.*, **39**, 593 (1972).
 (9) Fenby, D. V., Billing, G. J., Smythe, D. B., *J. Chem. Thermodyn.*, **5**, 49 (1973).
 (10) Hale, J. D., Izatt, R. M., Christensen, J. J., *J. Phys. Chem.*, **67**, 2605 (1963).
 (11) Hsu, K.-Y., Clever, H. L., *J. Chem. Eng. Data*, **20**, 268 (1975).
 (12) Hsu, K.-Y., Clever, H. L., *J. Chem. Thermodyn.*, in press.
 (13) Kehiaian, H. V., *J. Chim. Phys. Phys.-Chim. Biol.*, **68**, 935 (1971).
 (14) Kehiaian, H. V., Sosnkowska-Kehiaian, K., Hryniewicz, R., *J. Chim. Phys. Phys.-Chim. Biol.*, **68**, 922 (1971).
 (15) Kertes, A. S., Grauer, F., *J. Phys. Chem.*, **77**, 3107 (1973).
 (16) Kentamaa, J., Lindberg, J. J., Nissema, A., *Suom. Kemistil. B*, **34**, 102 (1961).
 (17) Krishnan, C. V., Friedman, H. L., *J. Phys. Chem.*, **73**, 1572 (1969).
 (18) Lau, C. F., Wilson, P. T., Fenby, D. V., *Aust. J. Chem.*, **23**, 1143 (1970).
 (19) Lindberg, J. J., Kentamaa, J., Nissema, A., *Suom. Kemistil. B*, **34**, 98 (1961).
 (20) Monk, P., Wadso, I., *Acta Chem. Scand.*, **22**, 1842 (1968).
 (21) Murakami, S., Fujichiro, R., *Bull. Chem. Soc. Jpn.*, **39**, 720 (1966).
 (22) O'Donnell, J. F., Ayres, J. T., Mann, C. K., *Anal. Chem.*, **37**, 1161 (1965).
 (23) Stokes, R. H., Marsh, K. N., Tomlins, R. P., *J. Chem. Thermodyn.*, **1**, 211 (1969).
 (24) Vanderzee, C. E., Swanson, J. A., *J. Phys. Chem.*, **67**, 2608 (1963).

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The Ortho Effect. A Correlation Using Ebullioscopy

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Association of the solute benzoic acid and the ortho substituted benzoic acid solutes 2-bromo, 2-chloro, 2-methoxy, and 2-methyl in CCl₄ solutions was studied using ebullioscopy in the 0.04 to 0.4 m concentration range. Association numbers for solutes and observed equilibrium constants for solute dimerization reactions at 76.7 °C + ΔT_b at 1 atm pressure were calculated.

In this study the association of selected ortho substituted benzoic acid solutes and of benzoic acid in CCl₄ has been correlated with concentration and with the ortho substituent. The ortho effect has been primarily interpreted to be a steric effect; for ortho substituted benzoic acids the substituent may force the carboxyl group out of the plane of the benzene ring, decrease the resonance of the molecule, and affect the activity of the carboxyl group (δ). There are, however, very little reliable experimental data relating association of benzoic acids in aprotic solvents with the ortho substituent (2, 4). Correlation of data has been extremely difficult due to variations of solvent, temperature, and especially concentration. In this present study ortho substituents chosen for comparison, and where only intermolecular association is involved, are the chloro, bromo, and methyl groups. The effect of the ortho group on association can be quantitatively compared independent of steric differences for the chloro and methyl groups since their van der Waals radii are virtually the same at 1.75 and 1.72 Å, respectively (1). For these latter ortho groups, the group which causes the greatest increase in carboxyl bond polarity through inductive and resonance effects should most enhance hydrogen bonding between solute molecules, as indicated by increased intermolecular association. An ortho group such as methoxy, which can form an intramolecular hydrogen bond with the carboxyl group can be expected to have decreased intermolecular association due to this effect. The influence of such a group on intermolecular association must be considered separately from ortho groups which do not involve intramolecular association.

Experimental Section

The apparatus used has been previously described (7) and consisted of an improved Cottrell ebullioscope (3). All mea-

surements made use of a second apparatus with solvent only to correct for pressure fluctuations. In this study the lowest concentrations measured were approximately 0.04 m; below this concentration the temperature elevation became less than 0.100° and the Beckmann differential thermometers used measured only two significant figures. The upper concentration in the study was about 0.4 m to ensure solute solubility. The approximately one order of magnitude concentration range studied permitted study of association which is primarily interpreted as solute dimerization. Chemicals were reagent grade and were carefully checked for purity by melting point or boiling point and refractive index measurements before use. All solution concentrations were determined from careful weighings of solute and solvent.

Results and Discussion

Figure 1 shows the association of the solutes studied in CCl₄ where the association number, i , the ratio of the measured solute molecular weight to the true solute molecular weight, is plotted as a function of solution molality. It can be seen from the figure that choice of the concentration for purposes of comparison between solutes is significant. At approximately 0.10 m, for example, solute association number is close to 2.00 for chloro and bromo substituted benzoic acids whereas for the methyl substituted benzoic acid and for benzoic acid, association at this concentration is approximately 13% less than 2.00. Association at 0.10 m indicates a greater ionic character to the carboxyl-carboxyl bond for solutes with chloro and bromo ortho groups as compared with the methyl group; this greater ionic character may be primarily attributed to the inductive effect of the chloro and bromo ortho groups. The association shown in the figure demonstrates that, for the chloro and bromo ortho groups compared with benzoic acid at approximately 0.10 m any steric effect of the groups has not caused a decrease in association. In the case of the ortho methoxy group the figure shows that at almost all concentrations the intermolecular association is less than for benzoic acid, a fact that may be attributed to intramolecular hydrogen bonding.

Table I shows experimental results, including observed equilibrium constants in mole fraction concentration units, K_X ,