standard since there is only a deviation of 0.04% between our value and the value used, 0.8925×10^{-6} $m^2 \cdot s^{-1}$ (*11*).

Moreover, although chromatograms of others' "pure" hydrocarbons have shown impurities in greater concentration, the viscosity value of these compounds remains closer to the TRC Tables than the heptane value.

In the future, it is recommended that measurements on the viscosity of heptane be improved in order to use it as a standard.

Beyond the interest of knowing the kinematic viscosities and densities of new binary systems, the purpose of this work is to get numerous data in order to extend the table of interaction parameter values of the UNIFAC-VISCO model presented in a previous paper (*12*). Therefore, we have chosen to study numerous systems with a small number of mole fractions for each one. The experimental variable used in the UNIFAC-VISCO model is the excess molar free energy of activation of flow. Therefore, the validity of our measurements has been checked comparing experimental values of this variable to the literature values for hexane-hexadecane, hexane-tetradecane, and hexadecane-tetradecane systems. Figure 1 shows good agreement between our values and those of the literature. As regards the values of Dymond and Young (*13*), the mean deviation of the present values is of 0.17%, whereas the values of Heric and Brewer (*9*) show a mean deviation of 1.12%.

The validity of the UNIFAC-VISCO model for the present systems has been checked by the authors in a previous paper (*12*). The McAllister model imposes the experimental determination of two adjustable parameters and necessarily leads to a better estimation of the viscosity than the UNIFAC-VISCO model, which is completely predictive.

Glossary

Co	density-meter constant
k	viscometer constant
M	molecular weight
T	period
t	flow time
x	mole fraction
V^E	excess volume
v	Hagenbach correction
ρ	density
ν	kinematic viscosity
ν_{12}, ν_{21}	parameters of eq 3

Subscripts

1,2	components 1 and 2

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Excess Molar Enthalpies of Seven Benzene + *n*-Alkylamine Binary Liquid Mixtures

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An isobaric and quasi-isothermic calorimeter has been used to determine excess molar enthalpies, H^E, as a function of concentration at atmospheric pressure for seven binary mixtures containing an *n*-alkylamine (propyl-, butyl-, hexyl-, octyl-, decyl-, or dodecylamine, at 303.15 K, or pentadecylamine, at 313.15 K) with benzene. H^E of propylamine + benzene is positive, then, it decreases, and after reaching a minimum for butylamine, it increases with the chain length of the higher *n*-alkylamines.

Introduction

Following our study of thermodynamic properties on binary mixtures containing *n*-alkylamines (*1-4*), we report here the excess molar enthalpy, H^E, at 303.15 K, for benzene (C_6H_6) + propylamine ($PrNH_2$), + butylamine ($BuNH_2$), + hexylamine ($HeNH_2$), + octylamine ($OcNH_2$), + decylamine ($DeNH_2$), and + dodecylamine ($DcNH_2$) and for C_6H_6 + pentadecylamine ($PeNH_2$) at 313.15 K. As far as we know, the only previous measurements on these mixtures are those of Velasco et al. (*5*) of H^E for C_6H_6 + $PrNH_2$ and + $HeNH_2$ and Letcher and Bayles (*6*) for C_6H_6 + $BuNH_2$; their results of H^E of C_6H_6 + $PrNH_2$ are in very good agreement with ours, but they are higher than ours for C_6H_6 + $BuNH_2$ and + $HeNH_2$.

Experimental Section

All the *n*-alkylamines were the same as those used previously (*1*) as were their purification methods and physical properties. Benzene was from Fluka AG Buchs, better than 99.8 mol %.

Excess molar enthalpies were determined by using an isobaric and quasi-isothermic calorimeter similar to that described in ref 7. Electrical energy was measured to better than 0.5%, and temperature in the water bath was controlled to within

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Table I. Excess Molar Enthalpies (H^E) for Benzene + *n*-Alkylamine at 303.15 K as a Function of the Mole Fraction *x* of the *n*-Alkylamine

x	H^E, J mol^{-1}	x	H^E, J mol^{-1}	x	H^E, J mol^{-1}
		n-$C_3H_7NH_2$ + C_6H_6			
0.0449	105	0.3985	576	0.6382	543
0.0829	197	0.4583	588	0.7289	456
0.1321	290	0.5013	593	0.8371	311
0.1971	392	0.5351	596	0.9078	200
0.2493	455	0.5531	590	0.9517	109
0.2966	512	0.5868	568		
		n-$C_4H_9NH_2$ + C_6H_6			
0.0401	103	0.4016	579	0.7512	404
0.0770	188	0.4260	586	0.8407	284
0.1507	327	0.4912	591	0.9190	157
0.2347	450	0.5525	564	0.9547	85
0.3334	543	0.5898	550		
0.3342	546	0.6470	504		
		n-$C_6H_{13}NH_2$ + C_6H_6			
0.0408	109	0.4530	585	0.7510	401
0.0825	212	0.4659	583	0.7646	379
0.1543	353	0.5004	583	0.8314	278
0.2347	453	0.5391	578	0.8940	185
0.3307	538	0.5453	576	0.9499	85
0.3957	574	0.6005	550		
0.4410	590	0.6701	488		
		n-$C_8H_{17}NH_2$ + C_6H_6			
0.0331	120	0.3576	621	0.5424	589
0.0633	218	0.3927	630	0.6015	548
0.0973	302	0.4452	628	0.7010	447
0.1620	447	0.4501	631	0.7867	339
0.2404	546	0.4946	622	0.8566	236
0.3092	599	0.5130	610	0.9111	146
0.3270	604	0.5332	591	0.9554	69
		n-$C_{10}H_{21}NH_2$ + C_6H_6			
0.0319	128	0.3496	663	0.6370	543
0.0667	253	0.3513	661	0.7088	453
0.1000	345	0.3938	672	0.8036	323
0.1492	468	0.4103	676	0.8444	249
0.2300	587	0.4573	661	0.8976	167
0.3024	641	0.4892	652	0.9473	85
0.3057	642	0.5537	610		
		n-$C_{12}H_{25}NH_2$ + C_6H_6			
0.0324	152	0.3588	721	0.7351	444
0.0648	275	0.3991	723	0.7960	361
0.0995	391	0.4564	710	0.8914	207
0.1677	560	0.4949	694	0.9528	93
0.2371	657	0.5505	654		
0.3039	705	0.6403	564		
		n-$C_{15}H_{31}NH_2$ + C_6H_6[a]			
0.0309	175	0.2927	740	0.5877	632
0.0647	325	0.3406	746	0.6953	502
0.1001	442	0.3450	745	0.7837	377
0.1656	608	0.4035	737	0.8980	177
0.2385	708	0.4929	708		

[a] At 313.15 K.

±0.002 K. The estimated errors are $\partial x < 0.0002$; ∂T(reproducibility) = 0.01 K (*8*). The calorimeter was checked against hexane + cyclohexane, at 298.15 K, the agreement with the data reported (*9*) being better than 0.5% over the central range of concentration.

Results and Discussion

The H^E values are listed in Table I. The composition dependence of H^E was correlated by the polynomial

$$H^E_{\text{calc}}/(\text{J mol}^{-1}) = x(1-x)\sum_{i=0}^{n} a_i(1-2x)^i \tag{1}$$

where x is the mole fraction of n-alkylamine. The a_i parameters were obtained by least squares and are collected in Table II, together with the standard deviations $\sigma(H^E)$ calculated as

$$\sigma(H^E) = [\sum(H^E - H^E_{\text{calc}})^2/(N-n)]^{1/2} \tag{2}$$

where N is the total number of measurements and n is the number of coefficients a_i.

Table II. Parameters a_i of Equation 1 for Benzene + *n*-Alkylamine and Standard Deviations $\sigma(H^E)$ at 303.15 K

mixture	a_0	a_1	a_2	a_3	$\sigma(H^E)$, J mol^{-1}
C_6H_6 +					
$C_3H_7NH_2$	2377	−131	66		5
$C_4H_9NH_2$	2335	−343			3
$C_6H_{13}NH_2$	2339	−281	−31	−416	4
$C_8H_{17}NH_2$	2447	−798	304	−380	4
$C_{10}H_{21}NH_2$	2580	−963	397	−527	4
$C_{12}H_{25}NH_2$	2743	−1208	756	−323	4
$C_{15}H_{31}NH_2$[a]	2792	−1261	1018	−1020	4

[a] At 313.15 K.

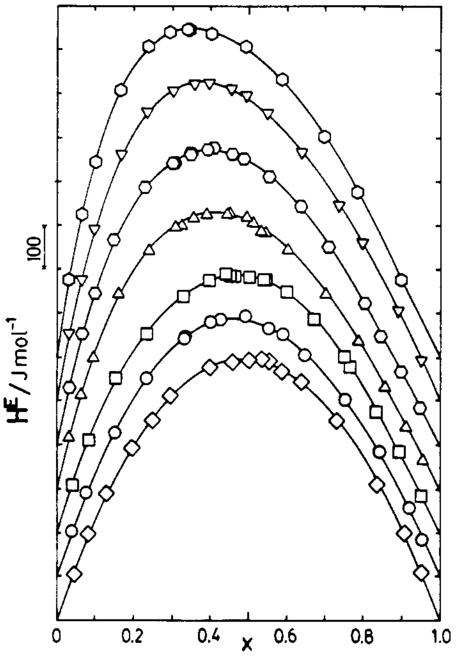

Figure 1. Excess molar enthalpies H^E(303.15 K) of C_6H_6 + (diamond) n-$C_3H_7NH_2$; (circle) n-$C_4H_9NH_2$; (square) n-$C_6H_{13}NH_2$; (triangle with point up) n-$C_8H_{17}NH_2$; (hexagon with flat top) n-$C_{10}H_{21}NH_2$; (triangle with point down) n-$C_{12}H_{25}NH_2$; (hexagon with pointed top) n-$C_{15}H_{31}NH$ (313.15 K) as a function of the mole fraction x of the n-alkylamine.

The H^E values are all positive (Figure 1) and decrease slightly from $PrNH_2$ to $BuNH_2$ and then increase with the chain length of the n-alkylamines. At the same time, the maxima of the H^E–x curves shift gradually toward the benzene-rich side. H^E of these mixtures show a noticeable exothermic effect compared to n-alkylamine + n-alkanes or + cyclohexane, which can be put down to the H_2N–π specific interaction.

Glossary

a_i	coefficients in eq 1
H^E	excess molar enthalpy, J mol^{-1}
x	mole fraction of n-alkylamine
n	number of coefficients in eq 1
$\sigma(H^E)$	standard deviation, eq 2, J mol^{-1}

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Potassium Sulfate Water–Alcohols Systems: Composition and Density of Saturated Solutions

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New data are presented for assessment of the crystallization of potassium sulfate by drowning-out precipitation. The solubility of potassium sulfate in water, in aqueous alcohols, and in aqueous acetone has been determined over the temperature range 15–35 °C, and the densities of the resulting saturated solutions have been measured. In all cases, the presence of either alcohol or acetone significantly reduces both the solubility of potassium sulfate in aqueous solution and the density of its saturated solution. The solubility data may conveniently be expressed by a relationship of the form ln $(w_{eq}) = A + Bx + Cx^2$ with an accuracy ∓2% where w_{eq} is the equilibrium saturation concentration of potassium sulfate, expressed as kilograms of potassium sulfate per kilogram of water, and x is the concentration of precipitant expressed as kilograms of organic cosolvent per kilogram water.

Introduction

Addition of an organic second solvent, or cosolvent, to induce drowning-out precipitation of soluble inorganic salts from aqueous solution has a number of potential advantages over alternative crystallization techniques since it creates the possibility of carrying out the operation at ambient temperature, yielding crystals of high purity.

Although the precipitation technique has been used for many years for production of fine crystals in the chemical and pharmaceutical industries, relatively few commercial and laboratory investigations have been reported in the literature (*1–9*).

Recently, complementary investigations of the continuous drowning-out precipitation of potassium sulfate (*10*) and potash alum (*11*) have clearly shown that it is possible to retrieve a crystal product that is close in filterability to that obtained by cooling crystallization.

The solubility of potassium sulfate in aqueous 2-propanol has been reported by Mydlarz et al. (*12*). The aim of this present work was to provide accurate solubility and density data for solutions of potassium sulfate in water, aqueous alcohols (methanol, ethanol), and aqueous acetone mixtures as an aid toward the assessment of the potential of drowning-out with alternative precipitants.

Experimental Section

The solubility of potassium sulfate in water–acetone and water–alcohol mixtures was determined by equilibrating crystals and solution in an agitated solubility cell (*12*, *13*). The experimental procedure is described in detail elsewhere (*12*). Briefly, the apparatus used for the solubility measurements was a 150-mL glass flask closed by a ground glass stopper and fitted with a magnetic stirrer. The cell was immersed in a thermostatic water bath controlled to ∓0.05 °C. The procedure is as follows. Volumetric quantities of twice-distilled water and analytical-grade cosolvent (BDH Chemical Ltd.; acetone, methanol, or ethanol with a minimum assay of 99.5%) are charged to the solubility cell. Then, the mass (in excess of saturation) of analytical-grade potassium sulfate crystals (BDH) is added to the solubility cell and agitated for a minumum of 1 h at a temperature at least 2 °C lower than the saturation temperature. The contents of the solubility cell are then agitated for at least 10 h at constant temperature. At the end of this time, the agitator is switched off, and, 1 h later, samples of clear solution are withdrawn and their density measured.

Solution concentration measurements were made by evaporating a sample to dryness, giving an estimated accuracy of $\mp 10^{-7}$ kg of K_2SO_4/kg of solution.

The densities of the various solutions were subsequently determined with a digital density meter (PAAR Model DMA 60), which gave a claimed precision of up to 10^{-7} g/cm^3.

The solubility and density of potassium sulfate–water solutions and potassium sulfate–water–organic cosolvent mixtures at temperatures of 15, 25, and 35 °C are listed in Table I. In all cases, both the solubility of potassium sulfate and the density of its saturated aqueous–precipitant solution are significantly reduced by the presence of the organic cosolvents. This behavior is illustrated for the new solubility data for potassium sulfate water–acetone mixtures at temperatures of 15, 25, and 35 °C shown in Figure 1.

The experimental solubility data are correlated by an expression of the form

$$\ln (w_{eq}) = A + Bx + Cx^2 \tag{1}$$

where w_{eq} is the equilibrium concentration of potassium sulfate

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