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Surface Tension of Binary Liquid Mixtures

M.C. SAXENA*, SHIPRA SIRCAR, MRS. MINU SAIGAL and MISS NISHI SINHA
Department of Chemistry,
K.S. Saket P.G. College, Faizabad 224 001, India

Surface tensions of pure organic liquids benzene, n-hexane and binary mixture of benzene + n-hexane have been evaluated at wide range of temperature and whole range of composition using Brock and Bird relation. The interaction has been explained on the basis of excess surface tension values.

INTRODUCTION

Several methods[1–8] have been proposed to predict the surface tension of pure liquids and liquid mixtures. In the present paper, semi-empirical relations given by Brock and Bird[9] for predicting surface tension of pure liquids have been extended to predict the surface tension of binary mixtures. Excess surface tension has been evaluated. Interactions have been discussed in the light of excess surface tension.

Theoretical

Brock and Bird[10] found the following correlations between the critical constants and surface tension.

$$\frac{\sigma}{(P_c^2T_c)^{1/3}} = \left(-0.951 + \frac{0.432}{Z_c}\right)(1 - T_r)^{11/9} \tag{1}$$

where P_c, T_c, Z_c and T_r are the critical pressure, critical temperature, critical compressibility factor and reduced temperature, respectively.

The critical compressibility factor and reduced temperature are given by the expressions

$$Z_c = \frac{P_cV_c}{RT_c} \tag{2}$$

$$T_r = \frac{T}{T_c} \tag{3}$$

where T and R stand for the absolute temperature and gas constant.

If the values of P_c, V_c, T_c of pure liquids are known one may easily evaluate the surface tension of liquids in the light of equations (1) to (3).

In the case of binary liquid mixtures the pseudocritical constant values can be taken and equation (1) can be written as

$$\frac{\sigma_{mix}}{(P_{c_m}^2 T_{c_m})^{1/3}} = \left(-0.951 + \frac{0.432}{Z_{c_m}}\right)(1 - T_{r_m})^{11/9} \tag{4}$$

These pseudocritical constant values P_{c_m}, T_{c_m} and V_{c_m} for binary liquid mixtures are calculated from the critical constants of pure liquids. The simplest procedure is to assume that P_{c_m}, T_{c_m} and V_{c_m} are all mole fraction averages, i.e.

$$P_{c_m} = X_1 P_{c(1)} + X_2 P_{c(2)}$$

$$T_{c_m} = X_1 T_{c(1)} + X_2 T_{c(2)}$$

$$V_{c_m} = X_1 V_{c(1)} + X_2 V_{c(2)} \tag{5}$$

Here X_1 and X_2 are the mole fractions of first and second components respectively. T_{r_m} and Z_{c_m} are given by the relation

$$T_r = \frac{T}{T_{c_m}} \tag{6}$$

and

$$Z_{c_m} = \frac{P_{c_m} V_{c_m}}{RT_{c_m}} \tag{7}$$

Thus if the values of critical constants of pure components are known, surface tension of binary liquid mixtures can be obtained using equation (4) in conjunction with equations (5), (6) and (7).

Surface tension of binary mixtures by ideal mixing rule may be given as

$$\sigma_{mix} = X_1\sigma_1 + X_2\sigma_2 \tag{8}$$

where X_1 and X_2 are the mole fractions of components 1 and 2 and σ_1 and σ_2 are the surface tensions of pure components 1 and 2.

The excess surface tension σ_E can be calculated from equation

$$\sigma_E = \sigma_{mix} - (\sigma_1 X_1 + \sigma_1 X_2) \tag{9}$$

The σ_E values are the direct measure of interaction in liquid mixture.

RESULTS AND DISCUSSION

The surface tension values of benzene and n-hexane have been evaluated at 298.15 K, 303.15 K, 308.15 K and 313.15 K using Brock and Bird relation (1). Surface tension of binary mixture of benzene + n-hexane at 298.15 K, 303.15 K, 308.15 K and 313.15 K has been evaluated using equation (4) and ideal mixing relation (8). The necessary data required for the calculation are taken from literature[11-15]. The results obtained are shown in Tables 1 to 3. Table 1 includes the critical constant values for the pure liquids. Table 2 includes the calculated and experimental values of surface tension for benzene and n-hexane at various temperatures, in columns fifth and seventh respectively. Column sixth includes surface tension obtained from Flory theory.[15]

TABLE 1
CRITICAL CONSTANTS FOR PURE LIQUIDS

Liquids	P_c (Atm)	V_c (litre $mole^{-1}$)	T_c (K)
Benzene	48.6	0.259	562.00
n-Hexane	29.9	0.370	507.20

TABLE 2
CALCULATED AND EXPERIMENTAL VALUES OF SURFACE TENSION OF PURE LIQUIDS AND THEIR RELATED PARAMETERS

Liquids	Temp. (K)	T_{r_m}	Z_{c_m}	σ dyne-cm^{-1} (eq (4))	σ dyne-cm^{-1} (Flory theory) (Ref. 15)	σ dyne-cm^{-1} (exptl.) (Ref. 15)
Benzene	298.15	0.5305	0.2729	27.55	26.09	28.15
	303.15	0.5394	0.2729	26.88	25.34	27.48
	308.15	0.5483	0.2729	26.28	24.88	26.81
	313.15	0.5572	0.2729	26.65	24.44	26.14
n-Hexane	298.15	0.5878	0.2658	17.53	17.42	17.94
	303.15	0.5976	0.2658	17.02	17.04	17.43
	308.15	0.6075	0.2658	16.51	16.63	16.90
	313.15	0.6174	0.2658	16.00	16.25	16.38

Table 3 includes surface tension of the binary mixtures of benzene and n-hexane obtained from Brock and Bird relation which has been given in column sixth of the table. The excess surface tension σ_E values are given in column seventh of this table.

An inspection of Table 2 shows that the surface tension values obtained for Brock and Bird relation which are given in column fifth, are in good agreement with the experimental results as compared to Flory theory, which are given in column VI of the table. The surface tension values follow the same decreasing trend with increase of temperature as the experimental values. This confirms the validity of the relation and the assumption on which its derivation is based.

A perusal of the column sixth of Table 3 shows that the surface tension values for the mixture show a regular increasing trend with the increasing mole fraction of benzene. A very remarkable point to note is that at the same mole fraction of benzene ($X_1 = 0.5955$), the surface tension values decrease with temperature (the value being 23.31 at 298.15 K, 22.74 at 303.15K, 22.15 at 308.15 K and 21.56 at 313.15 K). This is well in agreement with the effect of temperature on surface tension. The excess surface tension values are all positive (except that at $X_1 = 0.2959$ at 313.15 K it is negative and its magnitude is very low). The excess surface tension values σ_E are in increasing order with the increasing mole fraction of benzene, showing a clear interaction within the components. The regular decreasing value of surface tension for the mixture may be due to the fact that n-alkane molecules form random coils, due to internal rotation about carbon-carbon (C–C) bond. This tendency increases with the increase in the chain length of n-alkane. The presence of benzene molecules may put the n-alkane molecules under constraint and may decrease their coiling up. As a result, their entropy is decreased. Hence the molecules acquire their random configuration by moving to the surface. This accounts for the comparatively greater enrichment of the high surface tension, component, here benzene molecule in the binary system of benzene + n-hexane. Due to this reason positive excess surface tension values increase with mole fraction of benzene. The greater the magnitude of positive σ_E values, lesser is the Gibbson enrichment of the low surface tension component in the surface phase. Excess surface tension thus is a direct measure of interaction within the component, in the multicomponent system.

TABLE 3
EXCESS SURFACE TENSION OF BINARY MIXTURE OF BENZENE + HEXANE FROM BROCK AND BIRD RELATION

X_1	P_{c_m}	T_{c_m}	Z_{c_m}	T_{r_m}	σ dyne-cm^{-1} (Eq. (4))	σ_E dyne-cm^{-1} (Eq. (9))
T = 298.15 K						
0.2274	33.6163	519.6615	0.26746	0.57479	19.56	+0.1661
0.4239	37.4237	530.4297	0.26886	0.56354	21.56	+0.4654
0.5955	40.7527	539.8334	0.27008	0.55370	23.31	+0.7305
0.7465	43.6821	548.1082	0.27116	0.54516	24.89	+0.9946
0.8803	46.2778	555.4404	0.27211	0.53738	26.29	+1.2395
T = 303.15 K						
0.3239	35.4836	524.9497	0.26815	0.57881	19.98	+0.2544
0.5957	40.7566	539.8444	0.27009	0.56298	22.74	+0.7520
0.8154	45.0187	551.8840	0.27116	0.55016	24.99	+1.1872
T = 308.15 K						
0.4239	37.4236	530.4297	0.26886	0.58244	20.92	+0.2974
0.5955	40.7527	539.0334	0.27008	0.57227	22.15	+0.6046
0.7465	43.6821	548.1082	0.27116	0.56332	23.68	+0.8885
0.8803	46.2778	555.4404	0.27212	0.55540	23.04	+1.1517
T = 313.15 K						
0.2959	34.9404	523.4153	0.26795	0.59959	18.61	−0.0653
0.5955	40.7527	539.8334	0.27008	0.58166	21.56	+0.4385
0.8375	45.4475	553.0950	0.27181	0.56699	23.99	+0.8820

Thus it may be concluded that Brock and Bird relation may be used to find out the surface tension of liquids and their multicomponent system, without the botheration of finding the other parameters, as in other theories, provided the critical constants of pure components are known. This confirms the validity of the relation for liquids and its mixture and the assumption on which the theory is based. Since the excess surface tension is a direct measure of interaction within the component, the extent and magnitude of positive σ_E value is a measure of extent of interaction within the component.

Thus excess surface tension σ_E values may be used to predict the interaction within the component of a multi-component system.

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