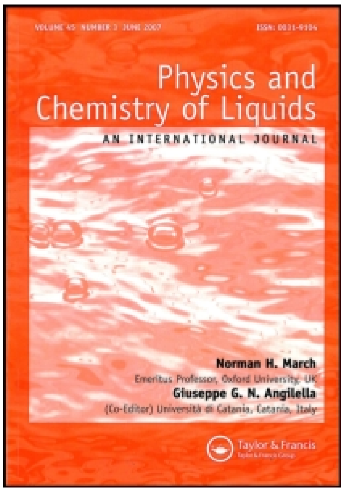

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S. K. Ray[a]; B. Mohanty[a]; S. Tripathy[b]; G. S. Roy[a]
[a] P.G. Department of Physics, Ravenshaw College, Cuttack, Orissa, India [b] B.J.B. College, Bhubaneswar, Orissa, India

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EVALUATION OF EXCESS GIBBS ENERGY OF MIXING IN BINARY MIXTURES OF DI-ISOBUTYL KETONE (DIBK) AND NONPOLAR SOLVENTS

S. K. RAY[a,]*, B. MOHANTY[a], S. TRIPATHY[b]
and G. S. ROY[a]

[a] *P.G. Department of Physics, Ravenshaw College, Cuttack-753 003, Orissa, India;* [b] *B.J.B. College, Bhubaneswar, Orissa, India*

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Excess Gibbs energy of mixing in binary mixture of Di-isobutyl ketone (DIBK) in nonpolar solvents namely *n*-heptane, *p*-xylene, cyclohexane, dioxane, benzene and tetrachloromethane have been evaluated at 303°K. The results indicate that $(\Delta G_{AB})_{\mathrm{maxima}}$ is in the order, *n*-heptane > *p*-xylene > cyclohexane > benzene > dioxane > tetrachloromethane.

Keywords: Binary mixtures; excess Gibbs energy of mixing; nonpolar liquid

INTRODUCTION

Liquid-liquid extraction process has become an important field of investigation in view of its application in separation and concentration process in analytical chemistry as well as its extensive use in the hydrocarbon industry for small scale laboratory operations. In the technological field, it also plays an important role in the processing of nuclear fuels and the production of some of the less common elements [1]. The mechanism associated with the solvent extraction process is

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*Corresponding author.

one of the simple complex formation where there appears two distinct phases in the product – an organic phase which contains the metal and an aqueous phase which contains the rest of product of the reaction. It is of interest to observe that when the concentration of the extracted species exceeds the solubility of the solvent in the organic system, a third phase appears at the interface of the organic and aqueous phase [2]. The third phase being a mixture of both organic and aqueous phase complicates the separation of organic phase which contains the nuclear metal. Thus the extractants in the pure form have low extraction efficiency. When the extractant is mixed with suitable diluents the physical properties of the system are altered and it helps in a better phase separation with consequent enhanced extraction efficiency [3]. When the extractant is blended with a diluent, the dielectric constant of the organic phase changes. Earlier [4] we have studied that the excess Gibbs energy of mixing in the binary mixture of polar–nonpolar liquids calculated from dielectric constant measurement is a measure of mixibility of the liquids and as such used as a powerful tool for studying molecular interaction in binary mixtures of polar–polar as well as polar–nonpolar liquids. In the present paper, we have evaluated excess correlation factor and excess Gibbs energy of mixing in the binary mixture of DIBK with non polar solvents to study the nature of molecular interaction and hence to know the extraction efficiency.

THEORY

Earlier [5, 6] we have defined the excess correlation factor in the binary mixture of polar and non polar liquids as

$$\delta g = g - (X_A + X_B g_B) \tag{1}$$

The excess Gibbs energy of mixing in the same binary mixture is defined as

$$\Delta G_{AB} = -\frac{N}{2}[R_{fB} - R^o_{fB}][X_B \mu^2_{gB}\{X_B(\delta g - 1) + 1\}] \tag{2}$$

where,

X_A and X_B	represent the mole fraction of nonpolar and polar liquids respectively,
V, V_A and V_B	denote the molar volume of the mixture, nonpolar liquid and polar liquid respectively,
ϵ, ϵ_A and ϵ_B	denote the dielectric constant of the mixture, nonpolar liquid and polar liquid respectively,
$\epsilon_{\infty B}$	represents the square of the refractive index of polar liquids,
μ_{gB}	represents the dipole moment of polar liquid,
k	is the Boltzmann constant,
T	is the temperature in Kelvin,
ϵ_o	is the vacuum permittivity,
N	is Avogadro's number,
g_B	is the correlation factor of pure polar liquid,
g	is Kirkwood correlation factor of the binary mixture,
R^o_{fB} and R_{fB}	are reaction field factor defined as

$$R^o_{fB} = \left[-\frac{2N}{9\,\epsilon_o\, V_B} \right] [((\epsilon_B - 1)(\epsilon_{\infty B} + 2)/(2\,\epsilon_B + \epsilon_{\infty B}))]$$

$$R_{fB} = \left[-\frac{2N}{9\,\epsilon_o\, V_B} \right] [((\epsilon - 1)(\epsilon_{\infty B} + 2)/(2\,\epsilon + \epsilon_{\infty B}))]$$

EXPERIMENTAL

The experimental device used for the measurement of dielectric constant, refractive index *etc.*, were same as used by Swain [7]. The accuracy of the measurement was also same. Measurements were taken at 303°K in the binary mixtures of DIBK in cyclohexane, *n*-heptane, benzene, tetrachloromethane, *p*-xylene, dioxane. All the chemicals used were of analytical grade (E. Merck, BDA) and were further purified by standard procedures [8].

RESULTS AND DISCUSSION

We have evaluated excess Gibbs energy of mixing ΔG_{AB} in the binary mixtures of DIBK and nonpolar solvents namely benzene, tetrachloromethane, *p*-xylene, dioxane, cyclohexane and *n*-heptane at 303°K, presented in Table I and displayed in Figure 1.

It is observed in Figure 1 that ΔG_{AB} remains positive throughout the concentrations of DIBK in the mixture. Initially ΔG_{AB} increases, attains a maxima at about 0.2 mole fraction of the polar liquid (DIBK) and thereafter falls approaching zero at mole fraction one of DIBK. The increasing trend of ΔG_{AB} is an indicator of the formation of β-clusters (*i.e.*, antiparallel alignment of molecular dipoles) in the mixture which results in reduction of internal energy of the system. DIBK is a mildly associated polar liquid. DIBK in its pure form is a

TABLE I Variation of excess correlation factor (δg) and excess free energy of mixing (ΔG_{AB}) in $\mathrm{J \cdot mol^{-1}}$ with the mole fraction of DIBK in nonpolar solvents at 303°K

X_B	δg	ΔG_{AB}	X_B	δg	ΔG_{AB}
	(a) DIBK + cyclohexane			(c) DIBK + benzene	
.105	−.445	137.95	.050	.072	63.07
.200	.038	159.78	.100	.264	98.34
.340	.169	145.26	.200	.278	123.18
.480	.101	107.53	.300	.232	119.72
.510	.074	94.06	.400	.186	109.37
.650	.126	60.16	.500	.190	86.60
.710	.102	45.39	.600	.244	70.30
.800	.092	25.81	.800	.072	20.24
.950	.048	1.29	.900	.016	6.09
	(b) DIBK + *n*-heptane			(d) DIBK + CCl_4	
.130	−.741	160.54	.050	.002	65.20
.210	−.269	188.32	.100	.274	101.31
.340	−.070	174.87	.200	.258	114.87
.450	−.022	141.15	.300	.272	109.74
.540	.022	128.71	.400	.286	105.06
.650	.076	71.01	.500	.250	77.87
.720	.106	55.29	.600	.314	65.27
.820	.080	28.28	.800	.112	20.00
.900	.068	11.31	.900	.086	5.89
	(e) DIBK + *p*-xylene			(f) DIBK + dioxane	
.100	−.784	113.74	.100	.844	74.57
.150	−.455	138.63	.190	.584	110.13
.200	−.359	181.30	.325	.298	115.78
.300	−.236	156.53	.480	.081	78.01
.390	−.098	136.25	.590	.099	59.23
.510	−.086	99.26	.650	.066	44.91
.650	−.104	51.80	.740	0.26	24.31
.720	−.083	35.84	.850	.094	15.39
.800	−.128	12.84	.960	0.52	1.70
.950	−.102	2.45			

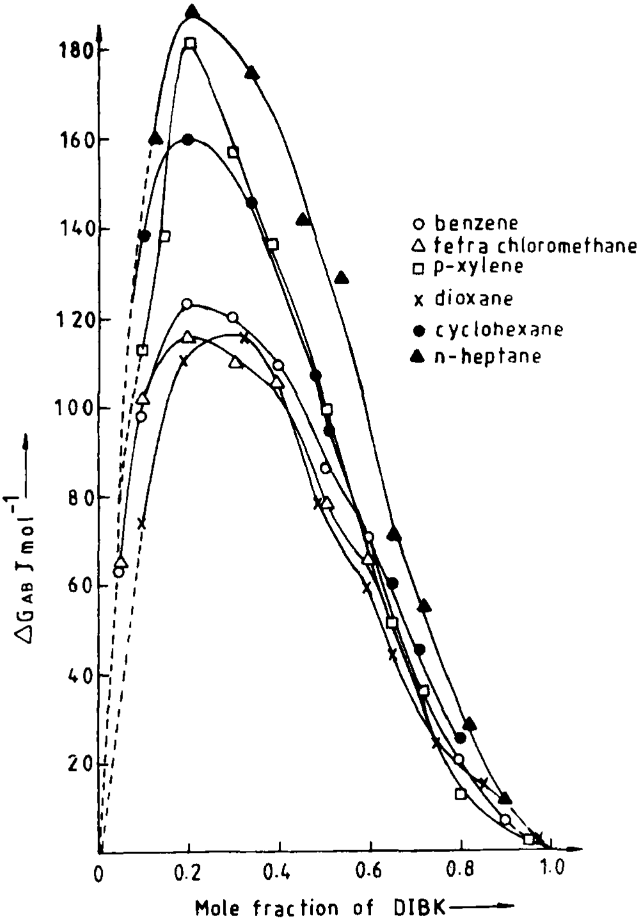

FIGURE 1 Variation of ΔG_{AB} in J mol^{-1} with the mole fraction of DIBK in the binary mixture of DIBK in nonpolar solvents at 303°K.

equilibrium mixture of keto and enol forms (Fig. 2) and hence there is a possibility of self-association in the pure liquid [9, 10]. The short range specific interaction between polar molecules leads to preferential dipolar alignment. Because of this, with increase in concentration of DIBK, there is gradual conversion of β-clusters to α-clusters. It results in increase of internal energy of the system and hence excess Gibbs energy of mixing decreases. Also in the higher concentration range of DIBK, the molecules of DIBK remain in wood-pile arrangement

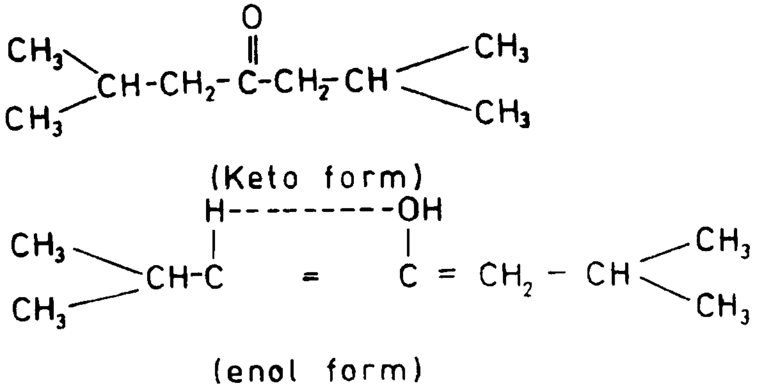

FIGURE 2 Equilibrium mixtures of two tautomers in DIBK.

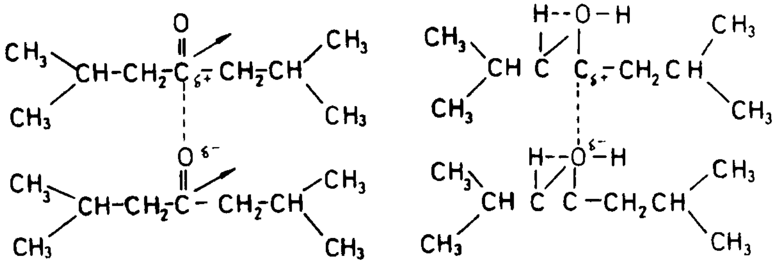

FIGURE 3 Wood pile arrangement in two tautomers of DIBK.

(Fig. 3) which favours the formation of α-clusters (parallel orientation of molecular dipoles) in the mixture [10].

It is observed that $(\Delta G_{AB})_{\mathrm{maxima}}$ in the binary mixtures are in the order, *n*-heptane > *p*-xylene > cyclohexane > benzene > dioxane > tetrachloromethane. We have earlier shown [4] that higher value of ΔG_{AB} is an indicator of less mixibility of the liquids and hence less molecular interaction between polar–nonpolar molecules in the mixture. The least interaction in case of *n*-heptane environment is due to its long chain structure. The maximum interaction in case of tetrachloromethane and DIBK molecules is facilited due to tetrahedral structure of relatively smaller molecules of tetrachloromethane. The relatively weak interaction between *p*-xylene and DIBK molecules are surrounded by predominant *p*-xylene molecules where the methyl group of *p*-xylene reduces the polar effect of DIBK. In DIBK and cyclohexane liquid mixture, DIBK molecules are trapped in the cleavage of boat and chair structure of cyclohexane molecules and the molecular interaction between the molecules are small. The molecular interaction between benzene and DIBK is facilited due to the presence of π-electron in the benzene molecule. In case of dioxane, there are two fold interactions. In the first situation, —OH of DIBK in its enol form probably establishes hydrogen bonding with oxygen of dioxane. In the second situation, $0^{\delta-}$ of $C{=}O$ group of DIBK in its keto form is likely to be influenced by the oxygen of dioxane resulting in breaking of intermolecular bonds in DIBK [10]. The second effect will overtake the first with slight increase of the mole fraction of DIBK as keto form is in excess of enol form. This leads to the molecular interaction between DIBK and dioxane molecules and consequently, excess Gibbs energy of mixing ΔG_{AB} is less in this case.

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